

- **CHEMICAL EQUILIBRIUM**
- **CHEMICAL BONDING**
- **S-BLOCK**
- **GASEOUS STATE**

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THEORY AND EXERCISE BOOKLET

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JEE SYLLABUS

• CHEMICAL EQUILIBRIUM

JEE - ADVANCED

Chemical equilibrium: Law of mass action; Equilibrium constant, Le Chatelier's principle (effect of concentration, temperature and pressure);

• CHEMICAL BONDING

JEE - ADVANCED

Orbital overlap and covalent bond; Hybridisation involving s, p and d orbitals only; Orbital energy diagrams for homonuclear diatomic species; Hydrogen bond; Polarity in molecules, dipole moment (qualitative aspects only); VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral).

• S-BLOCK

JEE - ADVANCED

Isolation/preparation and properties of the following non-metals: Boron, silicon, nitrogen, phosphorus, oxygen, sulphur and halogens; Properties of allotropes of carbon (only diamond and graphite), phosphorus and sulphur.

• GASEOUS STATE

JEE - ADVANCED

Gaseous and liquid states: Absolute scale of temperature, ideal gas equation; Deviation from ideality, van der Waals equation; Kinetic theory of gases, average, root mean square and most probable velocities and their relation with temperature; Law of partial pressures; Vapour pressure; Diffusion of gases.

CHEMICAL EQUILIBRIUM

Equilibrium

Basically, the term refers to what we might call a “balance of forces”. In the case of mechanical equilibrium, this is its literal definition. A book sitting on a table top remains at rest because the downward force exerted by the earth’s gravity acting on the book’s mass is exactly balanced by the repulsive force between atoms that prevents two objects from simultaneously occupying the same space, acting in this case between the table surface and the book. If you pick up the book and raise it above the table top, the additional upward force exerted by your arm destroys the state of equilibrium as the book moves upward. If you wish to hold the book at rest above the table, you adjust the upward force to exactly balance the weight of the book, thus restoring equilibrium. An object is in a state of mechanical equilibrium when it is either static or in a state of unchanging motion. From the relation $f=ma$, it is apparent that if the net force on the object is zero, its acceleration must also be zero, so if we can see that an object is not undergoing a change in its motion, we know that it is in **mechanical equilibrium**.

Another kind of equilibrium we all experience is **thermal equilibrium**. When two objects are brought into contact, heat will flow from the warmer object to the cooler one until their temperatures become identical. Thermal equilibrium is a “balance of forces” in the sense that temperature is a measure of the tendency of an object to lose thermal energy. A metallic object at room temperature will feel cool to your hand when you first pick it up because the thermal sensors in your skin detect a flow of heat from your hand into the metal, but as the metal approaches the temperature of your hand, this sensation diminishes. The time it takes to achieve thermal equilibrium depends on how readily heat is conducted within and between the objects; thus a wooden object will feel warmer than a metallic object even if both are at room temperature because wood is a relatively poor thermal conductor.

Chemical equilibrium

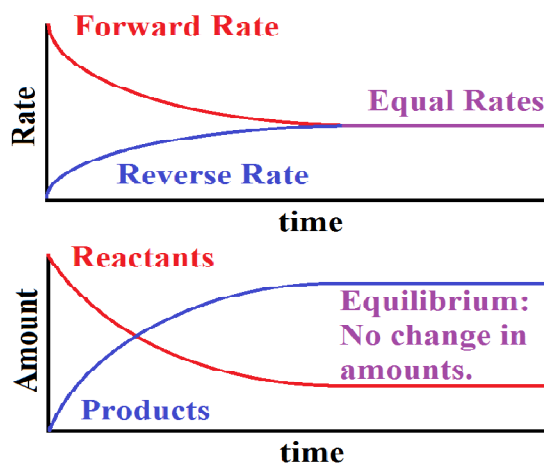
When a chemical reaction e.g. $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$ takes place in a closed container the quantities of components change as some are consumed and others are formed. Eventually this change will come to an end, after which the composition will remain unchanged as long as the system remains undisturbed. The system is then said to be in its equilibrium state, or more simply, “at equilibrium”.

It makes no difference whether we start with two moles of HI or one mole each of H_2 and I_2 ; once the reaction has run to completion, the quantities of these two components will be the same. In general, then, we can say that the composition of a chemical reaction system will tend to change in a direction that brings it closer to its equilibrium composition.

Dynamic equilibrium characteristics:

- The state at which concentrations of reactants or products do not change with time.
- It is attained when rate of forward reaction becomes equal to rate of backward reaction.
- A dynamic equilibrium, attained from either side.

CHEMICAL EQUILIBRIUM WITH GRAPH



Reversible reaction

A chemical equation of the form $A \rightarrow B$ represents the transformation of A into B, but it does not imply that all of the reactants will be converted into products, or that the reverse reaction $B \rightarrow A$ cannot also occur. In general, both processes can be expected to occur, resulting in an equilibrium mixture containing all of the components of the reaction system. If the equilibrium state is one in which significant quantities of both reactants and products are present then the reaction is said to be incomplete or reversible. In principle, all chemical reactions are reversible, but this reversibility may not be observable if the fraction of products in the equilibrium mixture is very small, or if the reverse reaction is kinetically inhibited.

Irreversible reactions

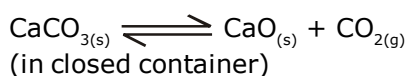
1. Unidirectional
2. Goes for completion
3. No equilibrium is attained
4. A reaction is said to be irreversible when either of the product is settled down as solid or escapes out as gas, e.g.,

$$\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + 2\text{NaCl}$$

$$\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)} \uparrow$$

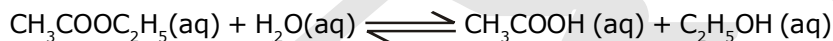
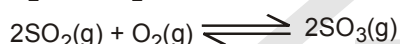
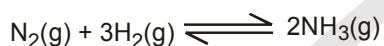
Reversible reactions

1. Both directional
2. Never goes for completion
3. Attains equilibrium
4. Otherwise the reaction is reversible e.g.,



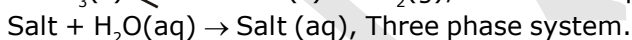
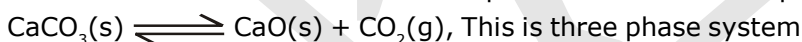
HOMOGENEOUS EQUILIBRIUM

The system in which all the reactant and product have same physical state.



HETEROGENEOUS EQUILIBRIUM

The system in which atleast one reactant or product have different physical states from others. eg.



LAW OF MASS ACTION

During the period 1864-1879 Cato Guldberg and Peter Waage showed that an equilibrium can be approached from either direction (see the hydrogen iodide illustration above), implying that any reaction $aA + bB \rightarrow cC + dD$ is really a competition between a "forward" and a "reverse" reaction. When a reaction is at equilibrium, the rates of these two reactions are identical, so no *net* (macroscopic) change is not observed, although individual components are actively being transformed at the microscopic level. Guldberg and Waage showed that the rate of the reaction in either direction is proportional to what they called the "active masses" of the various components:

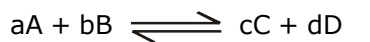
$$\text{rate of forward reaction} = k_f[A]^a[B]^b$$

$$\text{rate of reverse reaction} = k_r[C]^c[D]^d$$

in which the proportionality constants k are called *rate constants* and the quantities in square brackets represent concentrations. If we combine the two reactants A and B, the forward reaction starts immediately, but the formation of products allows the reverse process to get underway. As the reaction proceeds, the rate of the forward reaction diminishes while that of the reverse reaction increases. Eventually the two processes are proceeding at the same rate, and the reaction is at equilibrium: rate of forward reaction = rate of reverse reaction

$k_f[A]^a[B]^b = k_r[C]^c[D]^d$ If we now change the composition of the system by adding some C or withdrawing some A (thus changing their "active masses"), the reverse rate will exceed the forward rate and a change in composition will occur until a new equilibrium composition is achieved. The Law of Mass Action is thus essentially the statement that the equilibrium composition of a reaction mixture can vary according to the quantities of components that are present.

EQUILIBRIUM CONSTANT



At equilibrium, $R_f = R_b$

$$k_f[A]^a[B]^b = k_r[C]^c[D]^d \Rightarrow K_{eq} = \frac{k_f}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$K_c \rightarrow$ equilibrium constant in terms of concentration

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} \quad (K_p = \text{eq. constant in terms of partial pressure})$$

for the reaction, $N_2(g) + 3 H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}, \quad K_p = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3}$$

Law of Chemical Equilibrium

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the equilibrium Law or Law of Chemical Equilibrium

UNITS OF EQUILIBRIUM CONSTANT

The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure. unless the exponents of both the numerator and denominator are same.

For the reactions,

$H_2(g) + I_2(g) \rightleftharpoons 2HI$, K_c and K_p have no unit.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, K_c has unit mol/L and K_p has unit bar or atm

Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified. For a pure gas, the standard state is 1 bar. Therefore a pressure of 4 bar in standard state can be expressed as $4 \text{ bar}/1 \text{ bar} = 4$, which is a dimensionless number. Standard state (C_0) for a solute is 1 molar solution and all concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus in this system both K_p and K_c are dimensionless quantities and represented as K_p° & K_c° respectively

RELATION BETWEEN K_p AND K_c

For the reaction $aA + bB \rightleftharpoons cC + dD$

$$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$K_p = K_c (RT)^{\Delta n_g}$$

where $\Delta n_g = (c + d) - (a + b) = \text{no. of moles of gaseous products} - \text{no. of moles of gaseous Reactants}$

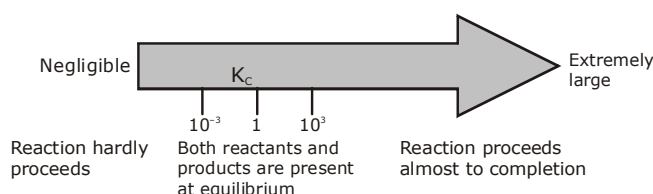
if $\Delta n = 0$ $K_p = K_c$

SIGNIFICANCE OF EQUILIBRIUM CONSTANT

(a) Using K_{eq} to Predict Relative Concentrations

The size of the equilibrium constant can give us information about the relative amounts of reactants and products present at equilibrium.

- **When $K \ll 1$**
The reaction lies to the left (mostly reactants)
- **When $K \gg 1$**
The reaction lies to the right (mostly products)
- **When $K = 1$**
The reaction lies in the middle (mix of reactants and products)

Dependence of extent of reaction on K_c

(b) Calculating Equilibrium concentrations

Ex. Phosgene is a poisonous gas that dissociates at high temperature into two other poisonous gases, carbon monoxide and chlorine. The equilibrium constant $K_p = 0.0041$ atm at 600K. Find the equilibrium composition of the system after 0.124 atm of COCl_2 initially is allowed to reach equilibrium at this temperature.

Sol.

	$\text{COCl}_2(\text{g})$	\rightleftharpoons	$\text{CO}(\text{g})$	$\text{Cl}_2(\text{g})$
initial pressures	0.124		0	0
change	-x		+x	+x
equilibrium pressures	0.124-x		x	x

Substitution of the equilibrium pressures into the equilibrium expression gives

$$\frac{x^2}{0.124 - x} = 0.0041$$

This expression can be rearranged into standard polynomial form $x^2 + 0.0041x - 0.00051 = 0$ and solved by the quadratic formula, but we will simply obtain an approximate solution by iteration.

Because the equilibrium constant is small, we know that x will be rather small compared to 0.124, so the above relation can be approximated by

$$\frac{x^2}{0.124} = 0.0041$$

which gives $x = 0.025$. **To see how good this is, substitute this value of x into the denominator of the original equation and solve again:**

$$\frac{x^2}{0.124 - 0.0225} = \frac{x^2}{0.102} = 0.0041$$

This time, solving for x gives 0.0204. Iterating once more, we get

$$\frac{x^2}{0.124 - 0.0204} = \frac{x^2}{0.104} = 0.0041$$

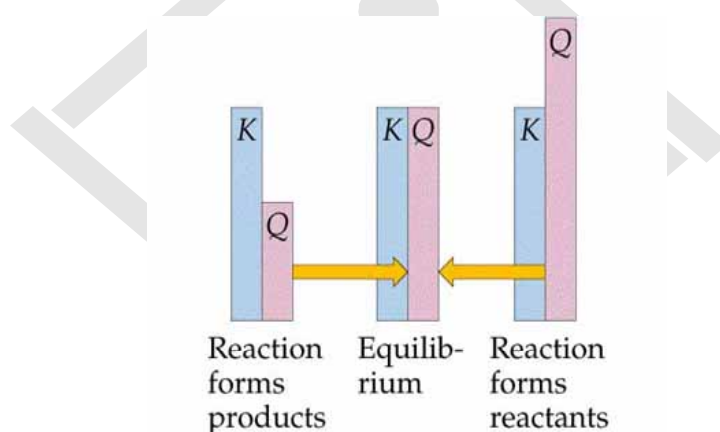
and $x = 0.0206$ which is sufficiently close to the previous to be considered the final result. The final partial pressures are then 0.104 atm for COCl_2 , and 0.0206 atm each for CO and Cl_2 .

Note: using the quadratic formula to find the exact solution yields the two roots -0.0247 (which we ignore) and 0.0206, which show that our approximation is quite good. *Note:* using the quadratic formula to find the exact solution yields the two roots -0.0247 (which we ignore) and 0.0206, which show that our approximation is quite good.

REACTION QUOTIENT (Q):

At each point in a reaction, we can write a ratio of concentration terms having the same forms as the equilibrium constant expression. The ratio is called the reaction quotient denoted by symbol Q. It helps in predicting the direction of a reaction.

The expression $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ at any time during reaction is called reaction quotient



- (i) if $Q > K_c$ reaction will proceed in backward direction until equilibrium is reached.
- (ii) if $Q < K_c$ reaction will proceed in forward direction until equilibrium is established.
- (iii) if $Q = K_c$ reaction is at equilibrium

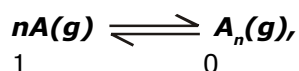
Ex. For the reaction $\text{NOBr (g)} \rightleftharpoons \text{NO (g)} + \frac{1}{2} \text{Br}_2(\text{g})$, $K_p = 0.15$ atm at 90°C . If NOBr, NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm & 2.0 respectively, will Br_2 be consumed or formed?

Sol. $Q_p = \frac{[P_{\text{Br}_2}]^{1/2} [P_{\text{NO}}]}{[P_{\text{NOBr}}]} = \frac{[0.20]^{1/2} [0.4]}{[0.50]} = 0.36$

$$K_p = 0.15$$

Hence, reaction will shift in backward direction, Therefore Br_2 will be consumed

DEGREE OF DISSOCIATION & VAPOUR DENSITY



1

0

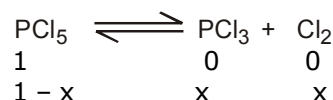
$$1 - \alpha \quad \frac{\alpha}{n}, \text{ moles of mix} = 1 - \alpha + \frac{\alpha}{n}$$

$$V.D. \propto \frac{1}{\text{moles}},$$

$$\frac{D_0}{d} = \frac{1 - \alpha + n\alpha}{1}, \text{ where } V.D. \text{ of } A = D_0, V.D. \text{ of eq. mix} = d$$

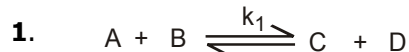
Ex. The Vapour Density of mixture of PCl_5 , PCl_3 and Cl_2 is 92. Find the degree of dissociation of PCl_5 .

Sol.



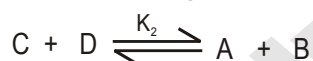
$$D_0 = \frac{208.5}{2} = 104.25, \quad \frac{104.25}{92} = 1 - \alpha + 2\alpha, \quad \alpha = 0.13$$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT



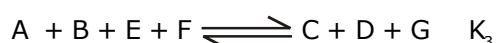
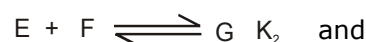
$$K_1 = \frac{[C][D]}{[A][B]}$$

After reversing the reaction



$$K_2 = \frac{[A][B]}{[C][D]} = \frac{1}{K_1}$$

After reversing the reaction the equilibrium constant get reversed.



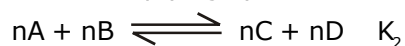
$$K_3 = \frac{[C][D][G]}{[A][B][E][F]} \Rightarrow K_3 = K_1 \times K_2$$

when the two reaction are added there equilibrium constant get multiplied.



$$K_1 = \frac{[C][D]}{[A][B]}$$

After multiplying by n



$$K_2 = \frac{[C]^n[D]^n}{[A]^n[B]^n} = K_1^n \Rightarrow K_2 = K_1^n$$

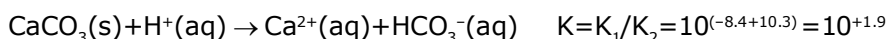
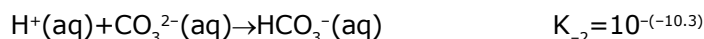
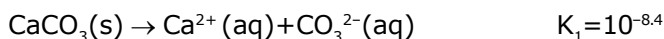
When the reaction is multiplied by any number then eq. constant gets the same number in its power.

Ex. Given the following equilibrium constants:



Calculate the value of K for the reaction $\text{CaCO}_3(\text{s}) + \text{H}^{+}(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{HCO}_3^{-}(\text{aq})$

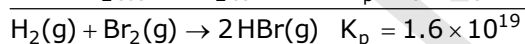
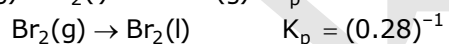
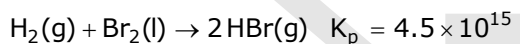
Sol. The net reaction is the sum of reaction 1 and the reverse of reaction 2:



Comment: This net reaction describes the dissolution of limestone by acid; it is responsible for the eroding effect of acid rain on buildings and statues. This is an example of a reaction that has practically no tendency to take place by itself (the dissolution of calcium carbonate) begin "driven" by a second reaction having a large equilibrium constant. From the standpoint of the LeChâtelier principle, the first reaction is "pulled to the right" by the removal of carbonate by the hydrogen ion. "Coupled" reactions of this type are widely encountered in all areas of chemistry, and especially in biochemistry, in which a dozen or so reactions may be linked in this way.

Ex. The synthesis of HBr from hydrogen and liquid bromine has an equilibrium constant $K_p = 4.5 \times 10^{15}$ at 25°C. Given that the vapor pressure of liquid bromine is 0.28 atm, find K_p for the homogeneous gas-phase reaction at the same temperature.

Sol: The net reaction we seek is the sum of the heterogeneous synthesis and the reverse of the vaporization of liquid bromine:



Here are some of the possibilities for the reaction involving the equilibrium between gaseous water and its elements:

$2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}(\text{g})$	$10 \text{H}_2 + 5 \text{O}_2 \rightarrow 10 \text{H}_2\text{O}(\text{g})$	$\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}(\text{g})$	$\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2 + 1/2 \text{O}_2$
$K_p = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 P_{\text{O}_2}}$	$K_p = \frac{P_{\text{H}_2\text{O}}^{10}}{P_{\text{H}_2}^{10} P_{\text{O}_2}^5}$	$K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{0.5}}$	$K_p = \frac{P_{\text{H}_2} P_{\text{O}_2}^{0.5}}{P_{\text{H}_2\text{O}}}$

EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

VAN'T HOFF EQUATION

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

where K is the equilibrium constant, T is temperature, ΔH is the enthalpy of the reaction and R is the gas constant. It provides means to determine how the equilibrium constant for a reaction or process will vary with temperature.

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Ex. $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$, $\Delta H = +13.7 \text{ kcal/mol}$, K_{eq} at $25^\circ\text{C} = 10^{-14}$. Calculate K_{eq} at 60°C ?

Sol. $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

$$\log \frac{K_2}{10^{-14}} = \frac{13.7}{2.303 \times 2 \times 10^{-3}} \left[\frac{1}{298} - \frac{1}{333} \right]$$

$$K_2 = 1.26 \times 10^{-12}$$

LECHÂTELIER PRINCIPLE

If a system at equilibrium is subjected to a change of pressure, temperature, or the number of moles of a substance, there will be a tendency for a net reaction in the direction that tends to reduce the effect of this change.

1. EFFECT OF CHANGE IN CONCENTRATION

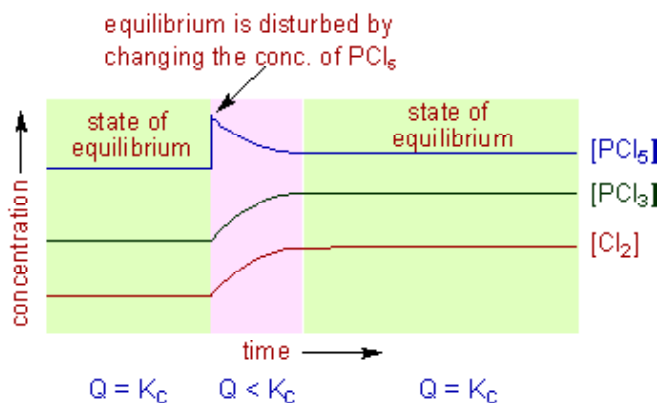
The change in concentration can affect gaseous systems or liquid solution systems only. However this does not affect the solid and pure liquid systems since their active masses are always taken as unity. By using Le Chatelier's principle, the effect of change in concentration on systems at equilibrium can be explained as follows:

1. When the concentration of reactant(s) is increased, the system tries to reduce their concentration by favoring the forward reaction.
2. When the concentration of product(s) is increased, the system tries to reduce their concentration by favoring the backward reaction.
3. When the concentration of reactant(s) is decreased, the system tries to increase their concentration by favoring the backward reaction.
4. When the concentration of product(s) is decreased, the system tries to increase their concentration by favoring the forward reaction.

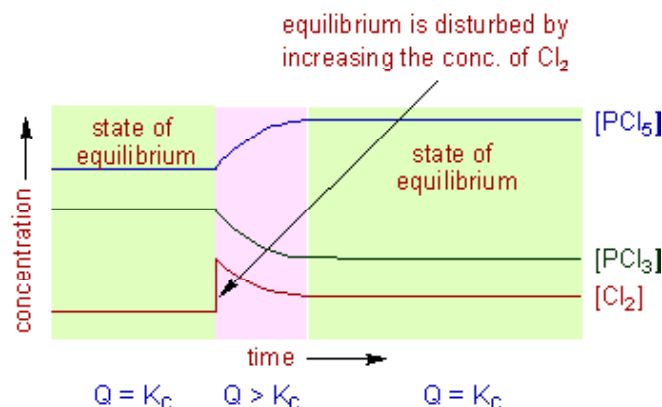
When the concentration of reactants is increased, the number of effective collisions between them increases which in turn increases the rate of forward reaction. Thus the forward reaction is more favored over the backward reaction until the new equilibrium is established. At this new equilibrium, the rates of both forward and backward reactions become equal again and the reaction quotient becomes approximately equal to the equilibrium constant.

Remember that small changes in concentration do not affect the equilibrium constant.

For decomposition reaction, $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$



Let the concentration of PCl_5 is doubled to disturb the equilibrium. This will change the reaction quotient, Q to: After disturbing the equilibrium, the value of Q becomes less than K_C . In order to restore the Q value to K_C , the concentration of PCl_5 must be decreased while the concentrations of PCl_3 and Cl_2 are to be increased. This is achieved by favoring the forward reaction.



The forward reaction is also favored by removing the products from the reaction mixture (decrease in the concentration of products). Upon removal of products, the rate of forward reaction becomes greater than that of backward reaction momentarily. This will also decrease the reaction quotient. Hence the system tries to reestablish the equilibrium by converting more reactants to products so as to make the rates of both forward and backward reactions become equal again.

For example, in case of the decomposition of PCl_5 , if the concentration of Cl_2 is increased by two times at equilibrium, the Q value becomes greater than the K_C value.

Hence the system tries to restore the value of Q to K_C again. The backward reaction is favored to decrease the concentration of Cl_2 . However the concentration of PCl_5 also decreases automatically while the concentration of PCl_3 increases while doing so.

2. EFFECT OF CHANGE IN PRESSURE

The change in pressure only affects the equilibrium of systems involving at least one gas. The Le Chatelier's principle can be applied to understand the effect of change in pressure on the systems at equilibrium as follows.

1. When the partial pressure of any of the gaseous reactants or of the products is increased, the position of equilibrium is shifted so as to decrease its partial pressure. This is usually achieved by favoring the reaction in which there is decrease in the number of moles of gaseous components.
2. When the partial pressure of any of the gaseous reactants or of the products is decreased, the position of equilibrium is shifted so as to increase its partial pressure. This can be achieved by favoring that reaction in which there is increase in the number of moles of gaseous components.

However, it is not always correct to say that the equilibrium is shifted whenever there is a change in the total pressure of the system. The equilibrium is not always disturbed upon changing the pressure of the entire system. It is only disturbed whenever there is a change in the partial pressure of any or all of the gaseous reactants or products in the equilibrium for which the $\Delta n_g \neq 0$. Where $\Delta n_g = (\text{no. of moles of gaseous products}) - (\text{no. of moles of gaseous reactants})$. Strictly speaking, the equilibrium is only shifted when the ratio of product of partial pressures of products to the product of partial pressures of reactants i.e., the reaction quotient in terms of partial pressures, Q_p is disturbed. The position of equilibrium is shifted so as to make Q_p become equal to the value of K_p again.

The Q_p can be changed in the following cases:

1. By adding or removing any gaseous reactant or product at constant volume. The effect is same as changing the concentration as explained above.
2. By changing the volume of the system (or in other words by changing the pressure of entire system) at equilibrium for which the $\Delta n_g \neq 0$. In this case, however, the pressure of the entire system is also changed.

For the decomposition of PCl_5 , the K_p can be written as: $K_p = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$

For this reaction $\Delta n_g = (1+1)-(1) = 1$

Hence for this reaction, if the pressure of the system is increased by 2 times by halving the volume, the reaction quotient, Q_p is doubled. In order to restore back the Q_p value again to K_p , the denominator value i.e., the partial pressure of PCl_5 must be increased. This is only achieved by favoring the forward reaction in which less number of gaseous products are formed. i.e., Two moles of products (PCl_3 and Cl_2) are converted to one mole of reactant (PCl_5)

Therefore we can say, if the pressure of the system is increased, the system tries to decrease it by favoring the reaction in the direction of decreasing the number of moles of gaseous components.

3. ADDITION OF INERT GAS

- (A) At constant volume : there is no effect of adding inert gas on the state of equilibrium at constant volume.
- (B) At constant pressure : On Adding of inert gas At constant pressure, the reaction proceeds in that direction where the sum of stoichiometric coefficient of gaseous components is greater.

4. EFFECT OF CHANGE IN TEMPERATURE

The effect of temperature can be understood by using Le Chatelier's principle as follows:

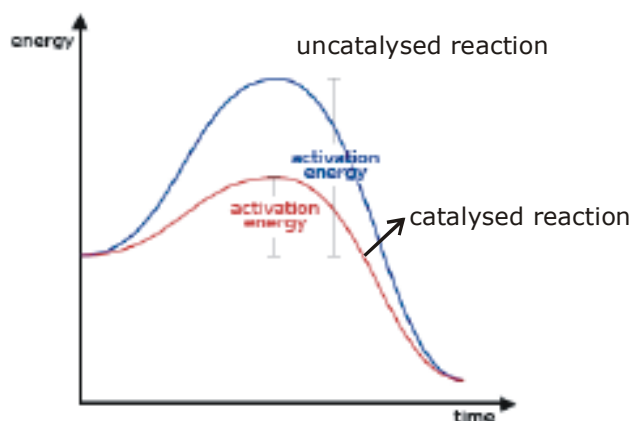
1. Increase in the temperature of the system favors the endothermic reaction. The increase in temperature increases the amount of heat in the system. Hence it tries to remove the excess of heat by favoring that reaction in which heat is absorbed i.e., the endothermic reaction.

2. Decrease in the temperature of the system favors the exothermic reaction. In this case, the temperature is decreased by removing the heat content from the system. Hence the system tries to restore the temperature back by favoring the exothermic reaction i.e., the reaction in which the heat is liberated.

It is very important to note that, during the change in temperature, the system establishes a new equilibrium for which the value of equilibrium constant is different from the original constant i.e., the equilibrium constant depends on the temperature.

EFFECT OF CATALYST

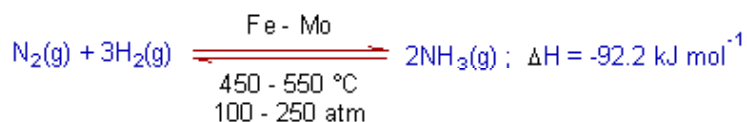
A catalyst has no effect on the position of the equilibrium since it increases not only the rate of forward reaction but also the rate of backward reaction. However it does help the system to reach the equilibrium faster.



INDUSTRIAL APPLICATIONS OF LE CHATELIER'S PRINCIPLE

1. HABER PROCESS

In Haber process, the ammonia is synthesized by combining pure nitrogen and hydrogen gases in 1:3 ratio in presence of finely powdered iron catalyst and molybdenum promoter at around 450°C and at about 250 atm. of pressure.



The le Chatelier's principle helps in choosing these conditions to improve the yields of ammonia as explained as below.

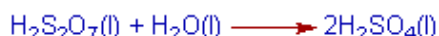
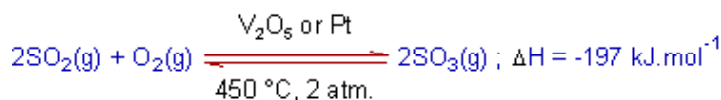
Effect of pressure:

Hence the synthesis of ammonia is favored by increasing the pressure of the system. Industrially, 100 - 250 atm. of pressure is employed. Effect of temperature: **Since the forward reaction is exothermic, the increase in temperature favors the backward reaction i.e., the dissociation of ammonia. That means according to le Chatelier's principle, the synthesis of ammonia is favored at lower temperatures.** However the reaction will be too slow at lower temperatures (a kinetic restriction). Hence this reaction is carried out at optimal temperatures i.e., at about 450 - 550 °C to overcome the kinetic barrier. Removal of ammonia: The forward reaction can also be favored by removing ammonia from the system from time to time by liquefying it. Catalyst: To increase the speed of the reaction, finely powdered or porous iron is used as catalyst. Its efficiency can be improved by adding molybdenum or oxides of potassium and aluminium.

The Percent by Mass of NH ₃ at Equilibrium in a Mixture of N ₂ , H ₂ , and NH ₃ as a Function of T and Total pressure			
Temperature (°C)	Total Pressure		
	300 atm	400 atm	500 atm
400	48% NH ₃	55% NH ₃	61% NH ₃
500	26% NH ₃	32% NH ₃	38% NH ₃
600	13% NH ₃	17% NH ₃	21% NH ₃

2. CONTACT PROCESS

In the contact process, sulfuric acid, the king of chemicals, is manufactured on large scale. The major steps involved in the process are:



The crucial step is the oxidation of sulfur dioxide, SO₂ to sulfur trioxide, SO₃. It is a reversible reaction. At normal conditions, the equilibrium lies far to the left and the amount of sulfur trioxide formed is very small. To improve the yield of sulfur trioxide, the reaction is carried out at around 450°C and 2 atm pressure in presence of V₂O₅ or Pt, which acts as a catalysts.

These conditions are chosen by applying Le Chatelier's principle as explained below.

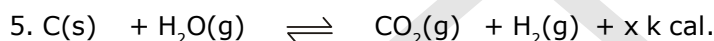
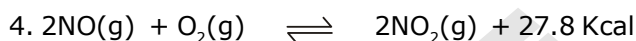
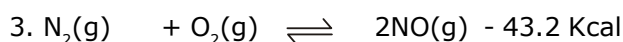
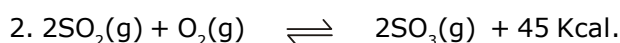
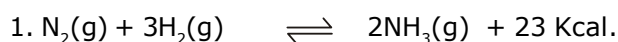
Effect of pressure: In the forward reaction (formation of sulfur trioxide), the number of moles of gaseous components is decreasing.

Hence the forward reaction is favored by increasing the pressure of the system. However, at high pressures, the iron towers used in the contact process are corroded. Hence the process is carried out at optimal pressures like 2 atm.

Effect of temperature: Since the forward reaction is exothermic, at higher temperatures the backward reaction i.e., the dissociation of sulfur dioxide is more favored. However the reaction will be too slow at lower temperatures. Hence this reaction is carried out at optimal temperatures i.e., around 450° C.

Catalyst: To increase the speed of the reaction, V_2O_5 or Pt are used as catalysts

Ex. Under what conditions will the following reactions go in the forward direction?



Sol.

- Low T, High P, excess of N_2 and H_2 .
- Low T, High P, excess of SO_2 and O_2
- High T, any P, excess of N_2 and O_2
- Low T, High P, excess of NO and O_2
- Low T, Low P, excess of C and H_2O
- High T, low P, excess of PCl_5
- High T, Low P, excess of N_2O_4

SIMULTANEOUS EQUILIBRIUM



Applicable only when at least one of the product is common in both the reaction.

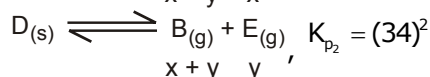
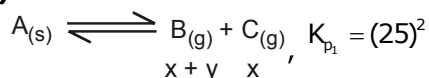
Ex. The pressure at equilibrium over solid A is 50 atm and over solid D is 68 atm if both solid A and D are heated simultaneously then find

(i) the total pressure over the solids.

(ii) In the above question find the mole ratio of C and B

(iii) mole fraction of C

Sol. (i)



$$K_{p_1} = (x + y) \times x \quad \dots(i)$$

$$K_{p_2} = (x + y) \times y \quad \dots(ii)$$

$$\text{total pressure} = p_B + p_C + p_E = x + y + x + y = 2(x + y)$$

$$\text{Also } K_{p_1} + K_{p_2} = (x + y)^2$$

$$\Rightarrow x + y = \sqrt{K_{p_1} + K_{p_2}}$$

$$\Rightarrow \text{Total pressure} = 2(x + y) = 2\sqrt{K_{p_1} + K_{p_2}}$$

- (ii) At constant temp and volume $P \propto n$
 \Rightarrow pressure Ratio will their mole ratio

$$\text{by eq. (i)/(ii)} \quad \frac{K_{p_1}}{K_{p_2}} = \frac{x}{y}$$

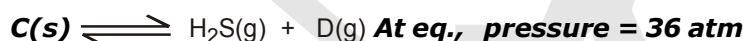
- (iii) Mole fraction of C

$$C = \frac{x}{2(x + y)}$$

$$\text{As we know } \frac{K_{p_1}}{K_{p_2}} = \frac{x}{y}$$

$$\Rightarrow \frac{y}{x} = \frac{K_{p_2}}{K_{p_1}} \Rightarrow \frac{x + y}{x} = \frac{K_{p_2} + K_{p_1}}{K_{p_1}}, \quad \frac{2(x + y)}{x} = \frac{2(K_{p_2} + K_{p_1})}{K_{p_1}}, \quad \frac{x}{2(x + y)} = \frac{K_{p_1}}{2(K_{p_2} + K_{p_1})}$$

$$\Rightarrow \text{mole fraction of C} = \frac{K_{p_1}}{2(K_{p_2} + K_{p_1})}$$

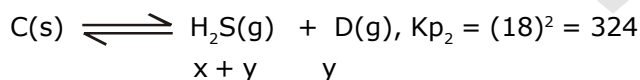
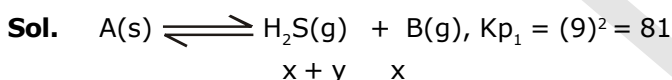


Calculation

(i) total pressure at new equilibrium when both the solids are heated simultaneously.

(ii) mole ratio of B and D

(iii) mole fraction of B in the mixture.



$$\text{total pressure} = x + y + x + y = 2(x + y)$$

$$K_{p_1} = x(x + y)$$

$$K_{p_2} = y(x + y)$$

$$\Rightarrow K_{p_1} + K_{p_2} = (x + y)^2 \Rightarrow x + y = \sqrt{K_{p_1} + K_{p_2}}$$

$$\Rightarrow \text{total pressure} = 2(x + y) = 2\sqrt{K_{p_1} + K_{p_2}} = 2\sqrt{81 + 324} = 2\sqrt{405} \text{ atm}$$

$$(ii) \text{ mole ratio of B \& D} = \frac{x}{y} = \frac{81}{324} = \frac{9}{108} = \frac{1}{12}$$

$$(iii) \text{ mole fraction of B in mixture} = \frac{x}{2(x + y)} = \frac{K_{p_1}}{2(K_{p_1} + K_{p_2})}$$

Heterogeneous reactions: the vapor pressure of solid hydrates

Many common inorganic salts form solids which incorporate water molecules into their crystal structures.

These water molecules are usually held rather loosely and can escape as water vapor. Copper(II) sulfate, for example forms a pentahydrate in which four of the water molecules are coordinated to the Cu^{2+} ion while the fifth is hydrogen-bonded to SO_4^{--} . This latter water is more tightly bound, so that the pentahydrate loses

water in two stages on heating: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow{140^\circ\text{C}} \text{CuSO}_4 \cdot \text{H}_2\text{O} \xrightarrow{400^\circ\text{C}} \text{CuSO}_4$

These dehydration steps are carried out at the temperatures indicated above, but at any temperature, some moisture can escape from a hydrate. For the complete dehydration of the pentahydrate we can define an equilibrium constant $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \rightarrow \text{CuSO}_4(s) + 5 \text{H}_2\text{O}(g)$ $K_p = 1.14 \times 10^{-10}$

The vapor pressure of the hydrate (for this reaction) is the partial pressure of water vapor at which the two solids can coexist indefinitely; its value is $K_p^{1/5}$ atm. If a hydrate is exposed to air in which the partial pressure of water vapor is less than its vapor pressure, the reaction will proceed to the right and the hydrate will lose moisture. Vapor pressures always increase with temperature, so any of these compounds can be dehydrated by heating. Loss of water usually causes a breakdown in the structure of the crystal; this is commonly seen with sodium sulfate, whose vapor pressure is sufficiently large that it can exceed the partial pressure of water vapor in the air when the relative humidity is low. What one sees is that the well-formed crystals of the decahydrate undergo deterioration into a powdery form, a phenomenon known as **efflorescence**. When a solid is able to take up moisture from

the air, it is described as **hygroscopic**. A small number of anhydrous solids that have low vapor pressures not only take up atmospheric moisture on even the driest of days, but will become wet as water molecules are adsorbed onto their surfaces; this is most commonly observed with sodium hydroxide and calcium chloride. With these solids, the concentrated solution that results continues to draw in water from the air so that the entire crystal eventually dissolves into a puddle of its own making; solids exhibiting this behavior are said to be **deliquescent**.

name	formula	vapor pressure, torr	
		25°C	30°C
sodium sulfate decahydrate	$\text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$	19.2	25.3
copper sulfate pentahydrate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	7.8	12.5
calcium chloride monohydrate	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$	3.1	5.1
(water)	H_2O	23.5	31.6

One of the first hydrates to be investigated in detail was calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$) which LeChâtelier showed to be what forms when the form of CaSO_4 known as plaster of Paris hardens; the elongated crystals of the hydrate bind themselves into a cement-like mass.

Ex. At what relative humidity will copper sulfate pentahydrate lose its waters of hydration when the air temperature is 30°C ? What is K_p for this process at this temperature?

Sol. From the table, we see that the vapor pressure of the hydrate is 12.5 torr, which corresponds to a relative humidity of $12.5/31.6 = 0.40$ or **40%**. This is the humidity that will be maintained if the hydrate is placed in a closed container of dry air.

For this hydrate, $K_p = P_{\text{H}_2\text{O}}^5$, so the partial pressure of water vapor that will be in equilibrium with the hydrate and the dehydrated solid (remember that *both* solids must be present to have equilibrium!), expressed in atmospheres, will be $(12.5/760)^5 = 1.20 \times 10^{-9}$.

RELATIONSHIP BETWEEN ΔG° & K

Free energy, G , denotes the self intrinsic electrostatic potential energy of a system. This means that in any molecule if we calculate the total electrostatic potential energy of all the charges due to all the other charges, we get what is called the free energy of the molecule. It tells about the stability of a molecule with respect to another molecule. Lesser the free energy of a molecule more stable it is. Every reaction proceeds with a decrease in free energy. The free energy change in a process is expressed by ΔG . If it is negative, it means that product have lesser G than reactants, so the reaction goes forward. If it is positive the reaction goes reverse and if it is zero the reaction is at equilibrium.

ΔG is the free energy change at any given concentration of reactants and products. If all the reactants and products are taken at a concentration of 1 mole per liter, the free energy change of the reaction is called ΔG° (standard free energy change).

One must understand that ΔG° is not the free energy change at equilibrium. It is free energy change when all the reactants and products are at a concentration of 1 mole/L. ΔG° is related to K (equilibrium constant) by the relation, $\Delta G^\circ = -RT \ln K$.

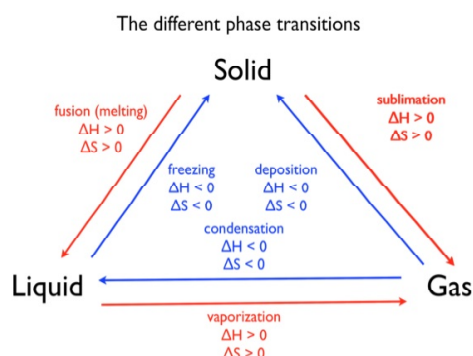
K may either be K_c or K_p . Accordingly we get ΔG_c° or ΔG_p° . The units of ΔG° depends only on R .

T is always in Kelvin, and if R is in Joules, ΔG° will be in joules, and if R is calories then ΔG° will be in calories.

PHYSICAL EQUILIBRIUM

PHASE TRANSITIONS

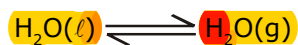
There are number of graphical means to help understand the relationships between the different phases of a particular substance. The first thing we need to do when looking at the transitions to different phases is to establish some definitions.



There are three particular phases between which we will be examining discrete phase changes. These are solids, liquids, and gases. Each transition has a particular name.

For example, the transition from liquid to gas is called vaporization. Vaporization is endothermic, and this transition leads to an increase in entropy. The reverse transition of a gas going to a liquid is condensation. Since condensation is simply the reverse of vaporization, the changes in enthalpy and entropy will be exactly the same, but opposite in sign. So $\Delta H_{\text{condensation}} = -\Delta H_{\text{vaporization}}$.

Let us consider the following physical equilibrium



1. Effect of temperature

Since it is an endothermic reaction, therefore reaction will proceed in forward direction on increasing temp. (Le Chatelier's principle)

2. Effect of pressure :

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

for the above equilibrium $\Delta H > 0$

ΔV ie $V_g - V_\ell = +ve$

$$\Rightarrow \frac{dP}{dT} = +ve$$

\Rightarrow on increasing P, T increases

But As reaction is to complete at the initial temp, therefore temperature must be lowered. This will make the reaction go to direction as suggested by Le-chatelier (endothermic reaction)

Ex. $A(s)$ ($d = 1.14 \text{ gm/cc}$)

$B(s)$ ($d = 1.5 \text{ gm/cc}$)



If mass of A and B are equal, on increasing the pressure, will for formation of B \uparrow or \downarrow ?

Sol. $A(s) \rightleftharpoons B(s)$

As density of solid B is greater than solid A, $V_B < V_A \Rightarrow V_B - V_A = -ve$

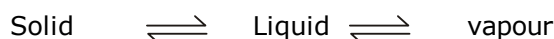
since reaction is exothermic, $\therefore \Delta H = -ve$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta H}{T\Delta V}, \frac{dP}{dT} = +ve$$

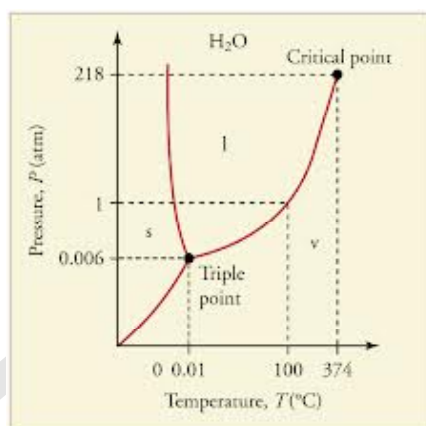
\Rightarrow **On increasing pressure, the rate of formation of B will be enhanced.**

LE CHATERLIER'S PRINCIPLE AND PHYSICAL EQUILIBRIUM

Consider physical equilibrium

**(i) Effect of pressure on melting**

When solid melts there is a decrease in volume for some solids (ice) and increase in volume for some solid (sulphur). When ice melts there is decrease in volume, So at constant volume there is a decrease in pressure. If pressure is increase as ice \rightleftharpoons water system, the equilibrium will go in forward direction. The above phenomena can also be explained from the following phase equilibrium diagram. If we see phase diagram for ice water system.



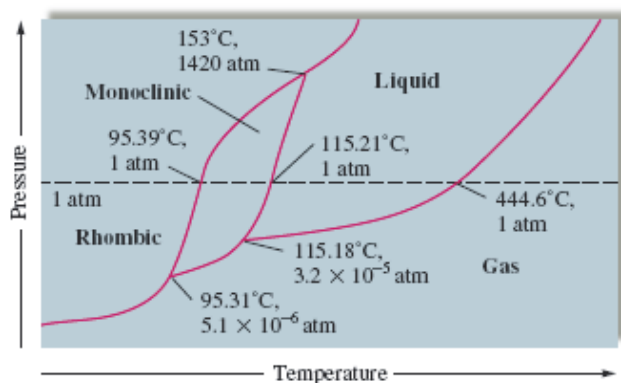
So on increasing pressure, melting point is increased so equilibrium is shifted in forward direction.

ii. Vapour pressure of liquids.

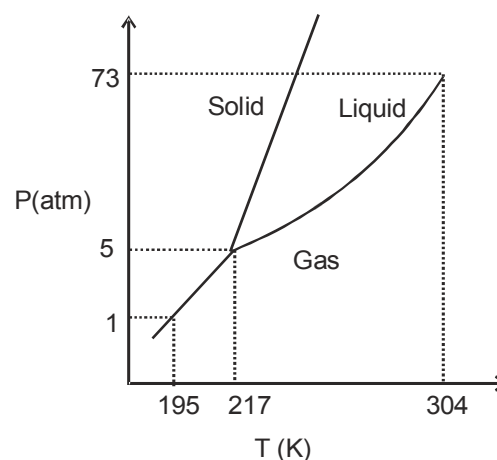
Consider liquid vapour equilibrium. Since evaporation of liquid is endothermic, hence rise in temperature will favour evaporation.

iii. Effect of temperature on solubility

If formation of solution is endothermic process then increase in temperature increases solubility. In formation of solution is exothermic then increase in temperature will lower the solubility.

PHASE DIAGRAM :

phase diagram of sulphur



Three phase diagram of CO₂

TRIPLE POINT

One very special point on a phase diagram is the triple point. This is the temperature and pressure at which three phases are in equilibrium. Typically, when we are talking about a triple point it is the solid, liquid, gas triple point. For CO_2 this is at a pressure of 5.11 atm and -56.4°C . Many substances have more than one solid phase, and therefore they can have more than one triple point.

CRITICAL POINT

If you follow the vaporization curve up to high temperature and pressure, you notice it simply stops. It is because this is the critical point (the on the diagram) for the substance. At temperatures and pressures greater than this point, the definition of a liquid and a gas disappear and the substance exists as a super-critical fluid (SCF). What is a super-critical fluid? It is a fluid (it takes the shape of its container) like a liquid and a gas, but it has a density that can vary between the two extremes of the liquid and the gas. This makes SCF extremely interesting. Typically, the molecules are either very close together or very far apart. In a SCF, they can essentially be anywhere in between.

What happens when you go from a gas to a SCF Essentially nothing. That is, the boundary between the liquid and the SCF and the gas and the SCF is an imaginary line defined by the critical point. This is not a phase transition. I repeat. Going from a gas to a SCF or a liquid to a SCF is not a phase transition. Going from a liquid to a gas, there is a discrete change in enthalpy, entropy, volume, density. This is a phase transition. When you "cross the line" from a gas to an SCF, there are no discrete changes. It is a continuous change. Thus, if the diagram shows this boundary, it is usually marked with dotted lines to note it is different.

Note: It is fairly easy to make CO_2 a SCF (relatively low temperature and pressure). As a result, it has wide industrial use as a SCF solvent.

SOLVED OBJECTIVE

Problem 1 : The enthalpies of two reactions are ΔH_1 and ΔH_2 both positive with $\Delta H_2 > \Delta H_1$. If the temperature of reacting system is increased from T_1 to T_2 predict which of the following alternative is correct ?

- (A) $\frac{k'_1}{k_1} = \frac{k'_2}{K_2}$ (B) $\frac{k'_1}{k_1} > \frac{k'_2}{K_2}$ (C) $\frac{k'_1}{k_1} < \frac{k'_2}{K_2}$ (D) $\frac{k'_1}{k_1} < \frac{k'_2}{K_2}$

Solution: As the temperature of reacting system is increased the equilibrium constant of reaction is also increased for endothermic reactions so for two reactions on increasing the temperature by equal amounts .

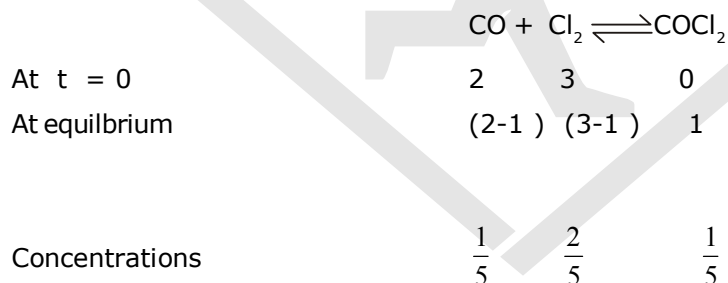
$$\frac{k'_1}{k_1} < \frac{k'_2}{K_2}$$

Ans. D

Problem 2: At a certain temperature 2 moles of carbon monoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$ in a 5 lit vessel. At equilibrium if one mole of CO is present then equilibrium constant for the reaction is :

- (A) 2 (B) 2.5 (C) 3.0 (D) 4

Solution:



$$K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{1/5}{\frac{1}{5} \times \frac{2}{5}} = \frac{25}{10} \text{ or } K_c = 2.5$$

Ans. B

Problem 3 : The numerical value of the equilibrium constant or any chemical change is affected by changing the

- (A) concentration of product (B) catalyst
(C) concentration of reacting substance (D) temperature

Solution : The equilibrium constant is unaffected by changing the concentration of products, catalyst and concentration of reactants. It is affected by changing the temperature.

Ans. D

Problem 4: The reaction : $3\text{O}_2 \rightleftharpoons 2\text{O}_3, \Delta H = + 69,000 \text{ calories}$ is aided by :

- (A) high temperature and low pressure
- (B) high temperature and high pressure
- (C) low temperature and high pressure
- (D) low temperature and low pressure

Solution : According to Le Chatelier principle formation of ozone is favoured by high temperature (endothermic reaction) and high pressure.

Ans. B

Problem5 : In the homogenous reaction $2\text{X}_2 + 2\text{Y}_2 \rightleftharpoons 2\text{X}_2\text{Y}_2$, ΔH is negative for forward direction. The mass of X_2Y_2 increased at equilibrium by

- (A) Raising the temperature
- (B) employing a suitable catalyst
- (C) reducing the total pressure
- (D) raising the total pressure

Solution: If the temperature is decreased and pressure is increased then reaction proceeds in forward reaction.

Ans. D

Problem6: The equilibrium constant at 323°C is 1000. What would be its value in the presence of a catalyst in the forward reaction.



- (A) 1000 x concentration of catalyst
- (B) 1000
- (C) $\frac{1000}{\text{concentration of catalyst}}$
- (D) impossible to tell

Solution: The equilibrium constant vary only with temperature. At constant temperature it will not vary.

Ans. B

Problem 7 : K_p for the reaction : $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ is found to be 160 at a given temperature. Originally equal number of moles of H_2 and CO_2 were placed in the flask. At equilibrium, the pressure of H_2 is 1.20 atm. What is the partial pressure of CO and H_2O ?

- (A) 4.80 atm each
- (B) 9.60 atm each
- (C) 2.40 atm each
- (D) 1.20 atm each

Solution: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$

$$K_p = \frac{P_{\text{CO}} \cdot P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} \cdot P_{\text{H}_2}}$$

$$P_{\text{CO}} \cdot P_{\text{H}_2\text{O}} = 16 \times 1.20 \times 1.20$$

$$P_{\text{H}_2\text{O}} \text{ or } P_{\text{CO}} = \sqrt{16 \times 1.20 \times 1.20} = 4.80 \text{ atm}$$

Ans. A

Problem 8: K_c for the reaction : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is 4.0×10^{-6} at 400 K. K_p for the above reaction is

- (A) 2.4×10^{-3} (B) 4.0×10^{-6}
 (C) $4 \times 10^{-6} \times (RT)^2$ (D) None of these

Solution: $N_2 + O_2 \rightleftharpoons 2NO$
 for this reaction $\Delta n = 0$

$$\text{Since } K_p = K_c(RT)^{\Delta n}$$

$$\therefore K_p = K_c$$

Ans. B

Problem-9: Which one of the following reactions at equilibrium, with all reactants and products in the gaseous phase, would be unaffected by an increase in pressure.

- (A) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (B) $2CO + O_2 \rightleftharpoons 2CO_2$
 (C) $2H_2 + O_2 \rightleftharpoons 2H_2O$ (D) $N_2 + O_2 \rightleftharpoons 2NO$

Solution: $N_2 + O_2 \rightleftharpoons 2NO$, the number of molecules of reactants and products are the same so it is not affected by the pressure.

Ans. D

Problem 10: For the gas phase reaction $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$, $\Delta H = -43.5$ kcal, which one of the following is true for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

- (A) K is independent of T (B) K decreases as T decreases
 (C) k increases as T decreases (D) K varies with addition of NO

Solution: The given reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is endothermic. Therefore, according to Le-Chatelier's Principle, high temperature favours forward reaction and hence K increase as T increase or K decrease as T decreases.

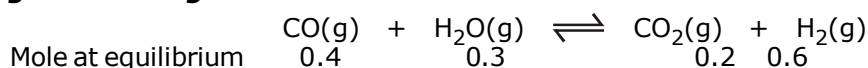
Ans. B

SOLVED SUBJECTIVE**1. An equilibrium mixture of**

$\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$
 present in a vessel of one litre capacity at 815°C was found by analysis to contain 0.4 mole of CO, 0.3 mole of H_2O , 0.2 mole of CO_2 and 0.6 mole of H_2 .

(a) Calculate K_C

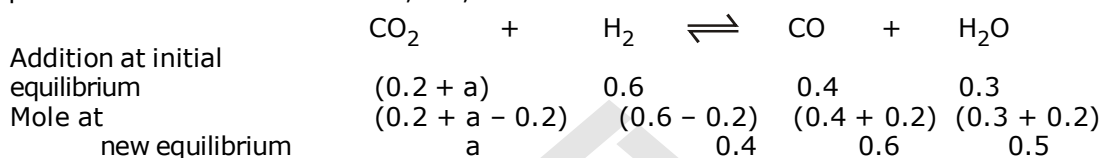
(b) If it is desired to increase the concentration of CO to 0.6 mole by adding CO_2 to the vessel, how many mole must be added into equilibrium mixture at constant temperature in order to get this change?

Sol.

$$(a) \quad \therefore K_C = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{0.2 \times 0.6}{0.4 \times 0.3} = 1$$

($\because \Delta n = 0$, \therefore Volume terms are not needed.)

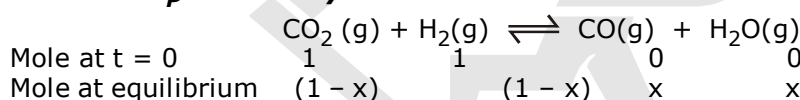
(b) Now it is desired to increase the conc. of CO by 0.2 at equilibrium by forcing CO_2 into equilibrium mixture. Suppose a mole of CO_2 are forced in vessel at equilibrium; by doing so reaction proceeds in backward direction, i.e.,



$$\therefore \frac{1}{K_C} = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{0.6 \times 0.5}{a \times 0.4}$$

$$\therefore a = 0.75 \text{ mole}$$

2. A mixture of one mole of CO_2 and one mole of H_2 attains equilibrium at a temperature of 250°C and a total pressure of 0.1 atm for the change $\text{CO}_2\text{(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{O(g)}$. Calculate K_P if the analysis of final reaction mixture shows 0.16 volume per cent of CO.

Sol.

Given that Vol. % of CO = 0.16

\therefore Mole of CO = x

$$\text{Total mole at equilibrium} = 1 - x + 1 - x + x + x = 2$$

$$\therefore \frac{x}{2} = \frac{0.16}{100}$$

$$\therefore x = 0.0032$$

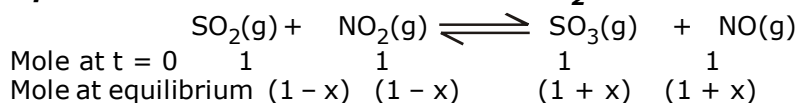
$$\text{Now, } K_C = K_P = \frac{x^2}{(1-x)^2} \quad (\because \Delta n = 0, \text{ volume terms are not needed})$$

$$K_P = \frac{(0.0032)^2}{(1-0.0032)} = 1.03 \times 10^{-5}$$

3. At a certain temperature, K_C for



is 16. If we take one mole of each of all the four gases in one litre container, what would be the equilibrium concentrations of NO and NO_2 ?

Sol.

$$\therefore K_c = \frac{\left(\frac{1+x}{V}\right)\left(\frac{1+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{(1+x)^2}{(1-x)^2}$$

$$\therefore \frac{(1+x)^2}{(1-x)^2} = 16 \quad (\therefore K_c = 16), \quad \frac{(1+x)}{(1-x)} = 4, \quad x = \frac{3}{5} = 0.6$$

$$\therefore [\text{SO}_2] = [\text{NO}_2] = 1 - x = 1 - 0.6 = 0.4 \text{ mol litre}^{-1} \text{ (Volume = 1 litre)}$$

$$[\text{SO}_3] = [\text{NO}] = 1 + x = 1 + 0.6 = 1.6 \text{ mol litre}^{-1}$$

4. At 627° C and one atmosphere pressure SO_3 is partially dissociated into SO_2 and O_2 by $\text{SO}_3(\text{g})$

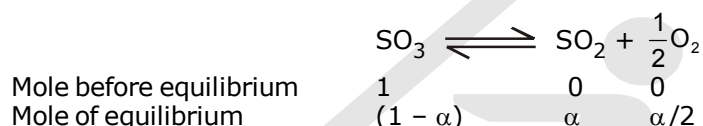
$\rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$. The density of the equilibrium mixture is 0.925 g/litre. What is the degree of dissociation?

Sol. For equilibrium mixture, $PV = \frac{w}{m}RT$, $\therefore M. wt_{\text{mixture}} = \frac{wRT}{VP}$

$$\therefore \frac{w}{V} = 0.925 \text{ g/L, } T = 900 \text{ K, } P = 1 \text{ atm, } R = 0.0821$$

$$M. wt_{\text{mixture}} = \frac{0.925 \times 0.0821 \times 900}{1} = 68.35$$

Experimental m. wt. of SO_3 mixture = 68.35, Nomral m.wt. of $\text{SO}_3 = 80$



$$\therefore \frac{\text{Normal m.wt.}}{\text{Apparent m.wt.}} = 1 + \frac{\alpha}{2}, \quad 1 + \frac{\alpha}{2} = \frac{80}{68.35}, \quad \alpha = 0.3408 \text{ or } 34.08\%$$

5. The equilibrium constant K_p of the reaction :



is 900 atm^{-1} at 800 K. A mixture containing SO_3 and O_2 having initial pressure of 1 atm and 2 atm respectively is heated at constant volume to equilibrate. Calculate partial pressure of each gas at 800 K at equilibrium.

Sol. $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$; $K_p = \frac{1}{900} \text{ atm}$

Initial pressure 1 0 2

Pressures left at $(1 - x)$ x $2 + \frac{x}{2}$

equilibrium

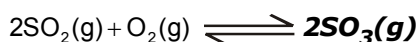
$$\therefore K_p = \frac{(P'_{\text{SO}_2})(P'_{\text{O}_2})}{(P'_{\text{SO}_3})^2} \Rightarrow \frac{1}{900} = \frac{x^2 \left(2 + \frac{x}{2}\right)}{(1-x)^2}$$

\therefore Since, K_p of this reaction is small and thus, $x \ll 1$, $\therefore x^3$ is negligible

$$\therefore \frac{1}{900} = \frac{x^2(2)}{(1-x)^2} = \frac{2x^2}{(1-x)^2}, \quad \frac{1}{30} = \frac{\sqrt{2}x}{(1-x)}, \quad x = 0.0236$$

$$P'_{\text{SO}_3} = 1 - x = 1 - 0.0236 = 0.9764 \text{ atm} \quad P'_{\text{SO}_2} = x = 0.0236 \text{ atm}, \quad P'_{\text{O}_2} = 2 + \frac{x}{2} = 2.0118 \text{ atm}$$

6. The equilibrium mixture for

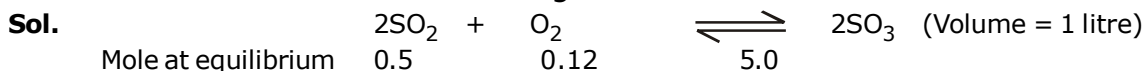


present in 1 litre vessel at 600°C contains 0.50, 0.12 and 5.0 mole of SO_2 , O_2 and SO_3 respectively.

(a) Calculate K_c for the given change at 600°C

(b) Also calculate K_p

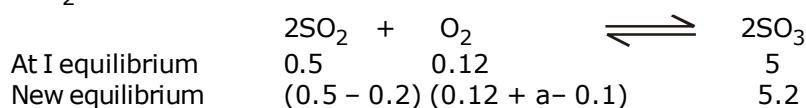
(c) How many mole of O_2 must be forced into the equilibrium vessel at 600°C in order to increase the concentration of SO_3 to 5.2 mole?



$$(a) K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(5)^2}{(0.5)^2(0.12)}, K_c = 833.33 \text{ mol}^{-1} \text{ litre}^1$$

$$(b) K_p = K_c (RT)^{\Delta n}, = 833.33 \times (0.0821 \times 873)^{-1} = 11.62 \text{ (atm)}^{-1}$$

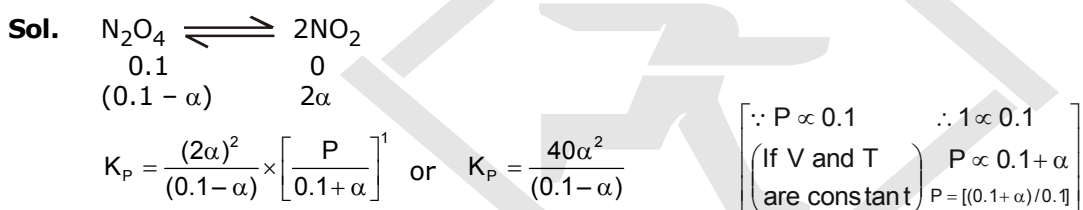
(c) Now O_2 is forced into the vessel in order to increase the concentration of SO_3 to 5.2 mole litre⁻¹. Let a mole of O_2 be introduced in it to increase SO_3 to 5.2 mole. Thus, 0.2 mole of SO_2 and 0.1 mole of O_2 will be consumed to show forward reaction.



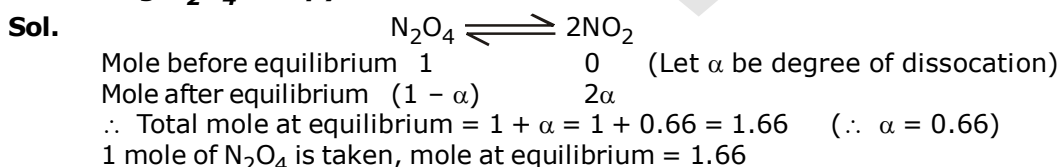
$$\therefore 833.3 = \frac{(5.2)^2}{(0.02 + a)(0.3)^2}, a = 0.34 \text{ mole}$$

7. 0.1 mole of $\text{N}_2\text{O}_4(\text{g})$ was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of $\text{NO}_2(\text{g})$ present, if the equilibrium.

is reached after some time.



$$\text{or} \quad \frac{40\alpha^2}{(0.1 - \alpha)} = 0.14, \alpha = 0.017, \text{ moles of } \text{NO}_2 = 0.017 \times 2 = 0.034 \text{ mole}$$

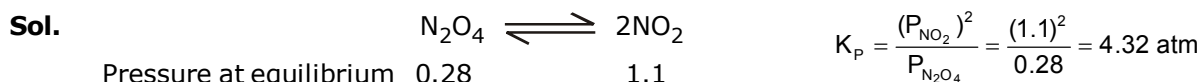
8. At 340 K and one atmospheric pressure, N_2O_4 is 66% dissociated into NO_2 . What volume of 10 g N_2O_4 occupy under these conditions?

$$\frac{10}{92} \text{ mole of } \text{N}_2\text{O}_4 \text{ is taken, mole at equilibrium} = \frac{1.66 \times 10}{92} = 0.18$$

$$\therefore PV = \frac{w}{m}RT, 1 \times V = 0.18 \times 0.0821 \times 340, V = 5.02 \text{ litre}$$

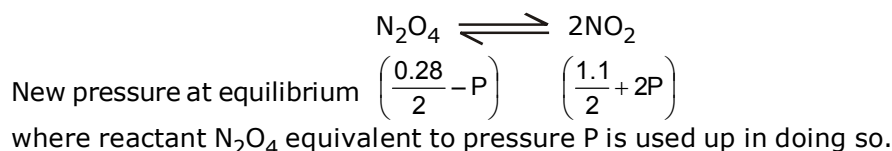
Thus, volume of 10 g N_2O_4 under above condition is 5.02 litre.

9. **An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atmosphere respectively. If the volume of container is doubled, calculate the new equilibrium pressure of two gases.**



∴

Now if volume of container is doubled i.e., pressure decreases and will become half, the reaction will proceed in the direction where the reaction shows an increase in mole, i.e., decomposition of N_2O_4 is favoured.



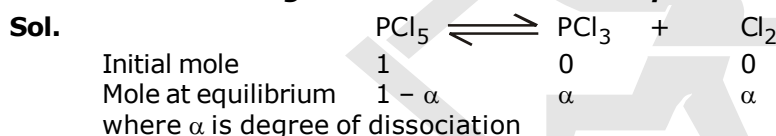
Again,

$$K_p = \frac{\left[\frac{1.1}{2} + 2P\right]^2}{\left[\frac{0.28}{2} - P\right]} = \frac{[0.55 + 2P]^2}{[0.14 - P]} = 4.32, P = 0.045, P_{N_2O_4} = 0.14 - 0.045 = 0.095 \text{ atm}$$

P_{NO_2} at new eq. = $0.55 + 2 \times 0.045$, $P_{NO_2} = 0.64 \text{ atm}$

10. **Prove $\alpha = \sqrt{\left(\frac{K_p}{P + K_p}\right)}$ for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$;**

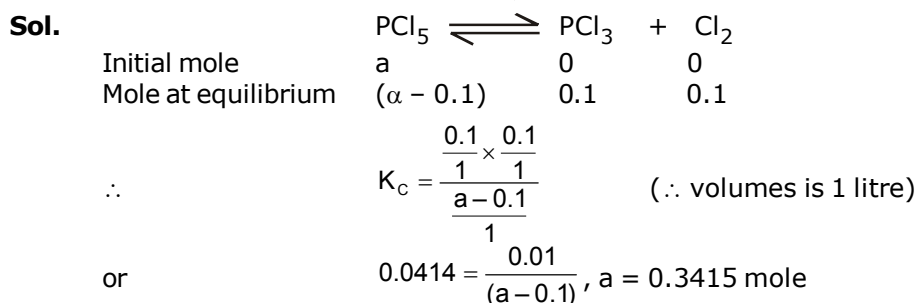
where α is degree of dissociation at temperature when equilibrium constant is K_p .



∴ $P'_{Cl_2} = \left[\frac{\alpha}{1 + \alpha}\right] \times P$; $P'_{PCl_3} = \left[\frac{\alpha}{1 + \alpha}\right] \times P$; $P'_{PCl_5} = \left[\frac{1 - \alpha}{1 + \alpha}\right] P$

∴ $K_p = \frac{P'_{PCl_3} \times P'_{Cl_2}}{P'_{PCl_5}} = \frac{\left[\frac{\alpha \times P}{1 + \alpha}\right] \left[\frac{\alpha \times P}{1 + \alpha}\right]}{\left[\frac{1 - \alpha}{1 + \alpha}\right] P} = \frac{\alpha^2 P}{1 - \alpha^2}$, $K_p = \frac{\alpha^2 P}{1 - \alpha^2}$, $\alpha = \sqrt{\left(\frac{K_p}{P + K_p}\right)}$ Hence proved.

11. **How much PCl_5 must be added to a one litre vessel at 250° in order to obtain a concentration of 0.1 mole of Cl_2 ? K_c for $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 0.0414 mol/litre.**



CLASS ROOM ASSIGNMENT

1. At 1300 K, and 1 atm pressure, A reaction was performed in 4 litre container as follows



If $K_c = 40$ and the mixture was supposed contain 2, 3 and 5 mole of SO_2 , O_2 and SO_3 respectively at any point of time of reaction. Then what will be the direction of the reaction?

Sol. reaction will proceed in forward direction

2. K_c for $\text{CO(g)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO}_2\text{(g)} + \text{H}_2\text{(g)}$ at 986°C is 0.63. A mixture of 1 mole $\text{H}_2\text{O(g)}$ and 3 mole of CO(g) is allowed to react to come to an equilibrium. The equilibrium pressure is 2.0 atm.

(i) How many moles of H_2 are present at equilibrium?

(ii) Calculate partial pressure of each gas at equilibrium?

Sol. (i) moles of H_2 formed = 0.681

(ii) (a) $P_{\text{H}_2} = 0.34 \text{ atm}$ (b) $P_{\text{CO}} = 1.16 \text{ atm}$ (c)

$P_{\text{H}_2\text{O}} = 0.16 \text{ atm}$

3. R.R.D. sir had a great interest in performing the experiment when he used to study at IT BHU. Once He saw the dissociation of PCl_5 and concluded that it was 40% dissociated at 4 atm. Calculate the pressure at which he will see 80% dissociation of PCl_5 , temperature remaining the same?

Sol. (0.43 atm)

4. The degree of dissociation of N_2O_4 in NO_2 at 7 atm and 37°C is 0.40. Calculate its K_p at 37°C . Also calculate the degree of dissociation at 25 atm pressure and at the same temp.?

Sol. $K_p = 5.33$, 22.3 %

5. For the reaction $2\text{NO(g)} \rightleftharpoons \text{N}_2\text{(g)} + \text{O}_2\text{(g)}$ and $\text{NO(g)} + \frac{1}{2}\text{Br}_2\text{(g)} \rightleftharpoons \text{NOBr(g)}$ values of K_c are respectively 2.4×10^{30} and 1.4. Determine K_c for the reaction $\frac{1}{2}$

$\text{N}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} + \frac{1}{2}\text{Br}_2\text{(g)} \rightleftharpoons \text{NOBr(g)}.$

Sol. 9.03×10^{-16}

6. Sulphide ion in alkaline solution reacts with solid sulphur to form polysulphide ions having formula S_2^{2-} , S_3^{2-} , S_4^{2-} and so on. The equilibrium constant for the formation of S_2^{2-} is 12, and for the formation of S_3^{2-} is 130, both from S and S^{2-} . Find the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S .

Sol. 10.83

7. In a gaseous reaction of the type $A + 2B \rightleftharpoons 2C + D$, the initial conc. of B was 1.5 times that of A. At equilibrium the equilibrium concentration of A and D were equal. Calculate the equilibrium constant.

Sol. $K_c = 4$

8. For the reaction $\text{NOBr(g)} \rightleftharpoons \text{NO(g)} + \frac{1}{2}\text{Br}_2\text{(g)}$; $K_p = 0.15 \text{ atm}$ at 90°C . If 0.5 atm of NOBr, 0.40 atm of NO and 0.2 atm of Br_2 are mixed at this temperature, will Br_2 be consumed or formed.

Sol. consumed

9. n moles of PCl_3 and n moles of Cl_2 are allowed to react at constant temperature T under a total pressure P as $\text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{PCl}_5\text{(g)}$. If y moles of PCl_5 are formed at equilibrium. Find K_p .

Sol. $\frac{(2n - y)y}{(n - y)^2 P}$

10. At temperature T , a compound $\text{AB}_2\text{(g)}$ dissociates according and the reaction $2\text{AB}_2\text{(g)} \rightleftharpoons 2\text{AB(g)} + \text{B}_2\text{(g)}$ with a degree of dissociation ' x '. Which is small compared to unity. Deduce the expression for ' x ' in terms of the equilibrium constant K_p and the total pressure P .

Sol. $x = \sqrt[3]{\frac{2K_p}{P}}$

11. Two gases A and B in the molar ratio 1 : 2 were admitted to an empty vessel and allowed to reach equilibrium at 400°C and 8 atm pressure as $A + 2B \rightleftharpoons 2C$, the mole fraction of C at equilibrium is 0.16. Calculate (a) K_p for the reaction, (b) The pressure at which mole fraction of A in equilibrium mixture is 0.16.

Sol. (a) 0.0064 atm^{-1} (b) 453.79 atm

12. 16 moles of hydrogen and 4 moles of nitrogen are sealed in a one litre vessel. The vessel is heated at a constant temperature until equilibrium is established, when it is found that the pressure in the vessel has fallen to 9/10 of its original value. Calculate K_c for the reaction $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$.

Sol. $6 \times 10^{-4} \text{ L}^2 \text{ mol}^{-2}$

13. Ammonia under a pressure of 15 atm at 27°C is heated to 347°C in a closed vessel in the presence of catalyst. Under these conditions NH_3 is partially decomposed according to the equilibrium $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$. The vessel is such that the volume remains effectively constant whereas pressure increases to 50 atm. Calculate the % NH_3 decomposed.

Sol. 30.65 %

- 14.** The ratio of the rate of diffusion of a sample of N_2O_4 partially dissociated into NO_2 with pure hydrogen was found to be 1:5. Calculate (a) the vapour density of the mixture (b) the degree of dissociation of N_2O_4 (c) % by volume of N_2O_4 in the mixture.

Sol.

- 15.** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. In this reaction, NO_2 is 20% of the total volume at equilibrium. Calculate (a) vapour density. (b) percentage dissociation of N_2O_4 .

Sol. (a) 41.4 (b) 11.11%

- 16.** For the reaction $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$ the K_c at $25^\circ C$ is 4×10^{-19} . Calculate $[Ag^+]$ in solution which was originally 0.1M in KCN and 0.03 M in $AgNO_3$.

Sol. 7.5×10^{-18}

- 17.** The progress of the reaction $A \rightleftharpoons n B$ with time t is shown in fig. Derive (a) the value of n (b) the equilibrium constant K_c . (c) the initial rate of conversion of A into products.

Sol. $n=2, K_c = 1.2, 0.1 \text{ M/hr}$

- 18.** For $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$, the observed pressure for reaction mixture in equilibrium is 1.12 atm at $106^\circ C$. What is the value of K_p for the reaction?

Sol. 0.3136 atm^2

- 19.** Some solid NH_4HS is placed in flask containing 0.5 atm of NH_3 . What would be pressures of NH_3 and H_2S when equilibrium is reached?

Sol. 0.6653 atm, 0.1653 atm

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g); K_p = 0.11$

- 20.** The equilibrium pressure of $NH_4CN(s)$ is allowed to decompose in pressure of NH_3 at 0.25 atm, calculate partial pressure of HCN at equilibrium.

Sol. 0.22 atm², 0.069 atm

- 21.** When 3.06 g of solid NH_4HS is introduced into a two-litre evacuated flask at 27°C . 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_c and K_p for the reaction at 27°C . (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

Sol. $8.1 \times 10^{-5} \text{ mol}^2 \text{ lit}^{-2}$, $4.9 \times 10^{-2} \text{ atm}^2$

- 22.** When 20 g of CaCO_3 were put into 10 litre flask and heated to 800°C , 35% of CaCO_3 remained unreacted at equilibrium. Calculate K_p for decomposition of CaCO_3 .

Sol. 1.145 atm

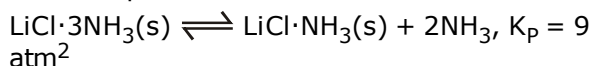
- 23.** Would 1% CO_2 in air be sufficient to prevent any loss in weight when M_2CO_3 is heated at 120°C ?



$K_p = 0.0095 \text{ atm}$ at 120°C .

Sol. 0.01 atm

- 24.** For the equilibrium :



at 40°C . A 5 litre vessel contains 0.1 mole of $\text{LiCl} \cdot \text{NH}_3$. How many mole of NH_3 should be added to the flask at this temperature to derive the backward reaction for completion?

Sol. 0.7837 mole

- 25.** Two solid compounds A and B dissociate into gaseous products at 20°C as



At 20°C pressure over excess solid A is 50 mm and that over excess solid B is 68 mm. Find :

- (i) The dissociation constants of A and B.
(ii) Relative numbers of mole of A' and B' in the vapour phase over a mixture of the solids A and B.

(iii) Show that the total pressure of gas over the solid mixture would be 84.4 mm.

Sol. (i) 1156 (mm)², (ii) 0.5407, (iii) 84.38 mm

EXERCISE – I

OBJECTIVE PROBLEMS (JEE MAIN)

1. For the reaction equilibrium :

$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$; the concentration of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol/L respectively. The value of K_c for the reaction is :

- (A) 3×10^{-3} M (B) 3×10^3 M
(C) 3.3×10^2 M (D) 3×10^{-1} M

Sol.

2. What is the equilibrium constant for the reaction $\text{P}_{4(\text{s})} + 5\text{O}_{2(\text{g})} \rightleftharpoons \text{P}_4\text{O}_{10(\text{s})}$:

- (A) $K_c = \frac{1}{[\text{O}_2]^5}$ (B) $K_c = \frac{[\text{P}_4\text{O}_{10}]}{5[\text{P}_4][\text{O}_2]^5}$
(C) $K_c = [\text{O}_2]^5$ (D) $K_c = \frac{[\text{P}_4\text{O}_{10}]}{[\text{P}_4][\text{O}_2]^5}$

Sol.

3. The equilibrium constant for the reaction :

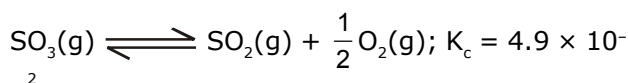
$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$ at temperature T is 4×10^{-4} . The value of K_c for the reaction.

$\text{NO}(\text{g}) \rightleftharpoons \frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ at the same temperature is :

- (A) 0.02 (B) 50
(C) 4×10^{-4} (D) 2.5×10^{-2}

Sol.

4. The equilibrium constant for the given reaction :



The value of K_c for the reaction :



- (A) 416 (B) 2.40×10^{-3}
(C) 9.8×10^{-2} (D) 4.9×10^{-2}

Sol.

5. For the following three reactions 1, 2 and 3, equilibrium constants are given :

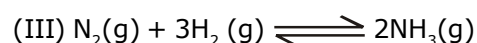
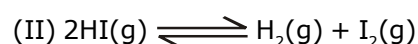


Which of the following relations is correct ?

- (A) $K_1 \sqrt{K_2} = K_3$ (B) $K_2 K_3 = K_1$
(C) $K_3 = K_1 K_2$ (D) $K_3 \cdot K_2^3 K_1^2$

Sol.

6. Consider following reactions in equilibrium with equilibrium concentration 0.01M of every species



Extent of the reactions taking place is :

- (A) $\text{I} > \text{II} > \text{III}$ (B) $\text{I} < \text{II} < \text{III}$
(C) $\text{II} < \text{III} < \text{I}$ (D) $\text{III} < \text{I} < \text{II}$

Sol.

7. A definite amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. NH_4HS decomposes to give NH_3 and H_2S and at equilibrium total pressure in flask is 0.84 atm. The equilibrium constant for the reaction is :
- (A) 0.30 (B) 0.18
(C) 0.17 (D) 0.11

Sol.

8. For the reaction $3\text{A(g)} + \text{B(g)} \rightleftharpoons 2\text{C(g)}$ at a given temperature, $K_c = 9.0$. What must be the volume of the flask, if a mixture of 2.0 mol each of A, B and C exist in equilibrium ?
- (A) 6 L (B) 9 L
(C) 36 L (D) None of these

Sol.

9. Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulas S_2^{2-} , S_3^{2-} , S_4^{2-} and so on. The equilibrium constant for the formation of S_2^{2-} is 12 (K_1) & for the formation of S_3^{2-} is 132 (K_2), both from S and S^{2-} . What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S
- (A) 11 (B) 12
(C) 132 (D) None of these

Sol.

10. 1 mole N_2 and 3 mol H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained.

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$. The equilibrium constant K_p for dissociation of NH_3 is :

- (A) $\frac{1}{0.5} \times (1.5)^3 \text{ atm}^{-2}$ (B) $0.5 \times (1.5)^3 \text{ atm}^2$
(C) $\frac{0.5 \times (1.5)^3}{3 \times 3} \text{ atm}^2$ (D) $\frac{3 \times 3}{0.5 \times (1.5)^3} \text{ atm}^{-2}$

Sol.

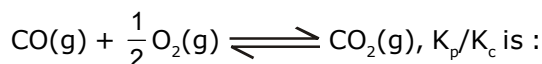
11. One mole of $\text{N}_2\text{O}_4(\text{g})$ at 300 K is left in a closed container under one atm. It is heated to 600 K when 20% by mass of $\text{N}_2\text{O}_4(\text{g})$ decomposes to $\text{NO}_2(\text{g})$. The resultant pressure is :
- (A) 1.2 atm (B) 2.4 atm
(C) 2.0 atm (D) 1.0 atm

Sol.

12. For the following gases equilibrium.
 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ K_p is found to be equal to K_c . This is attained when temperature is
 (A) 0°C (B) 273 K
 (C) 1 K (D) 12.19 K

Sol.

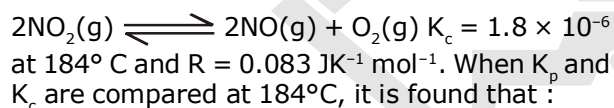
13. For the reaction :



- (A) RT (B) $(RT)^{-1}$
 (C) $(RT)^{-1/2}$ (D) $(RT)^{1/2}$

Sol.

14. For the reaction :



- (A) $K_p > K_c$ (B) $K_p < K_c$
 (C) $K_p = K_c$ (D) None of these

Sol.

15. PCl_5 dissociation a closed container as :



If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is α , the partial pressure of PCl_3 will be :

- (A) $P \cdot \left[\frac{\alpha}{\alpha+1} \right]$ (B) $P \cdot \left[\frac{2\alpha}{1-\alpha} \right]$
 (C) $P \cdot \left[\frac{\alpha}{\alpha-1} \right]$ (D) $P \cdot \left[\frac{\alpha}{1-\alpha} \right]$

Sol.

16. For the reaction : $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$, the degree of dissociated (α) of $\text{HI}(\text{g})$ is related to equilibrium constant K_p by the expression :

- (A) $\frac{1+2\sqrt{K_p}}{2}$ (B) $\sqrt{\frac{1+2K_p}{2}}$
 (C) $\sqrt{\frac{2K_p}{1+2K_p}}$ (D) $\frac{2\sqrt{K_p}}{1+2\sqrt{K_p}}$

Sol.

17. The equilibrium constant for the reaction

$\text{A}(\text{g}) + 2\text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g})$ is $0.25\text{ dm}^6\text{ mol}^{-2}$. In a volume of 5 dm^3 , what amount of A must be mixed with 4 mol of B to yield 1 mol of C at equilibrium.

- (A) 3 moles (B) 24 moles
 (C) 26 moles (D) None of these

Sol.

18. For the reaction

$\text{A}(\text{g}) + 2\text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g}); K_c = 10^{12}$ If the initial moles of A, B, C and D are 0.5, 1, 0.5 and 3.5 moles respectively in a one litre vessel. What is the equilibrium concentration of B ?

- (A) 10^{-4} (B) 2×10^{-4}
 (C) 4×10^{-4} (D) 8×10^{-4}

Sol.

19. The equilibrium constant K_c for the reaction,
 $A(g) + 2B(g) \rightleftharpoons 3C(g)$ is 2×10^{-3}
 What would be the equilibrium partial pressure of gas C if initial pressure of gas A & B are 1 & 2 atm respectively.
 (A) 0.0625 atm (B) 0.1875 atm
 (C) 0.21 atm (D) None of these

Sol.

20. A 20.0 litre vessel initially contains 0.50 mole each of H_2 and I_2 gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if $K_{eq} = 49$ for the reaction $H_2 + I_2 \rightleftharpoons 2HI$.
 (A) 0.78 M (B) 0.039 M
 (C) 0.033 M (D) 0.021 M

Sol.

21. A vessel of 250 litre was filled with 0.01 mole of Sb_2S_3 and 0.01 mole of H_2 to attain the equilibrium at $440^\circ C$ as
 $Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$.
 After equilibrium the H_2S formed was analysed by dissolving it in water and treating with excess of Pb^{2+} to give. 1.195 g of PbS (Molecular weight = 239) precipitate.
 What is value of K_c of the reaction at $440^\circ C$?
 (A) 1 (B) 2
 (C) 4 (D) None of these

Sol.

22. The equilibrium constant for the reaction
 $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 3 at 500 K. In a 2 litre vessel 60 gm of water gas [equimolar mixture of $CO(g)$ and $H_2(g)$] and 90 gm of steam is initially taken.
 What is the equilibrium concentration of $H_2(g)$ at equilibrium (mole/L) ?
 (A) 1.75 (B) 3.5
 (C) 1.5 (D) 0.75

Sol.

23. At $87^\circ C$, the following equilibrium is established
 $H_2(g) + S(s) \rightleftharpoons H_2S(g)$ $K_p = 7 \times 10^{-2}$
 If 0.50 mole of hydrogen and 1.0 mole of sulfur are heated to $87^\circ C$ in 1.0 L vessel, what will be the partial pressure of H_2S at equilibrium ?
 (A) 0.966 atm (B) 1.38 atm
 (C) 0.0327 (D) 9.66 atm

Sol.

24. At certain temperature (T) for the gas phase reaction
 $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$ $K_p = 12 \times 10^8$ atm
 If Cl_2 , HCl & O_2 are mixed in such a manner that the partial pressure of each is 2 atm and the mixture is brought into contact with excess of liquid water. What would be approximate partial pressure of Cl_2 when equilibrium is attained at temperature (T) ?
[Given : Vapour pressure of water is 380 mm Hg at temperature (T)]
 (A) 3.6×10^{-5} atm (B) 10^{-4} atm
 (C) 3.6×10^{-3} atm (D) 0.01 atm

Sol.

25. At 675 K, $\text{H}_2(\text{g})$ and $\text{CO}_2(\text{g})$ react to form $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, K_p for the reaction is 0.16.

If a mixture of 0.25 mole of $\text{H}_2(\text{g})$ and 0.25 mol of CO_2 is heated at 675 K, mole% of $\text{CO}(\text{g})$ in equilibrium mixture is :

- (A) 7.14 (B) 14.28
(C) 28.57 (D) 33.33

Sol.

26. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equilibrium.

- (A) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
(B) $\text{C}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g})$
(C) $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$
(D) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

Sol.

27. Change in volume of the system does not alter the number of moles in which of the following equilibrium

- (A) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
(B) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
(C) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
(D) $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

Sol.

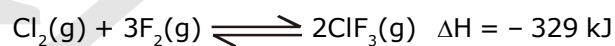
28. The conditions favourable for the reaction :

$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) ; \Delta H^\circ = -198 \text{ kJ}$
are :

- (A) low temperature, high pressure
(B) any value of T and P
(C) low temperature and low pressure
(D) high temperature and high pressure

Sol.

29. The exothermic formation of ClF_3 is represented by the equation :



Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2 , F_2 and ClF_3 :

- (A) Increasing the temperature
(B) Removing Cl_2
(C) Increasing the volume of container
(D) Adding F_2

Sol.

30. Densities of diamond and graphite are 3.5 and 2.3 gm/mL. respectively and for

$C(\text{diamond}) \rightleftharpoons C(\text{graphite}) \Delta H = -1.9 \text{ kJ/mole}$
favourable conditions for formation of diamond are

- (A) high pressure and low temperature
(B) low pressure and high temperature
(C) high pressure and high temperature
(D) low pressure and low temperature

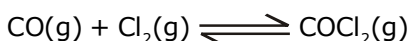
Sol.

31. The equilibrium $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is attained at 25°C in a closed rigid container and an inert gas, helium is introduced. Which of the following statements is/are correct.

- (A) concentrations of SO_2 , Cl_2 and SO_2Cl_2 do not change
(B) more chlorine is formed
(C) concentration of SO_2 is reduced
(D) more SO_2Cl_2 is formed

Sol.

32. Following two equilibrium is simultaneously established in a container



If some $\text{Ni}(\text{s})$ is introduced in the container forming $\text{Ni}(\text{CO})_4(\text{g})$ then at new equilibrium

- (A) PCl_3 concentration will increase
(B) PCl_3 concentration will decrease
(C) Cl_2 concentration will remain same
(D) CO concentration will remain same

Sol.

33. The yield of product in the reaction

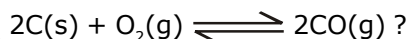


would be lower at :

- (A) low temperature and low pressure
(B) high temperature & high pressure
(C) low temperature and high pressure
(D) high temperature & low pressure

Sol.

34. What is the effect of the reduction of the volume of the system for the equilibrium



- (A) The equilibrium will be shifted to the left by the increased pressure caused by the reduction in volume
(B) The equilibrium will be shifted to the right by the decreased pressure caused by the reduction in volume.
(C) The equilibrium will be shifted to the left by the increased pressure caused by the increase in volume.
(D) The equilibrium will be shifted to the right by the increased pressure caused by the reduction in volume.

Sol.

35. The vapour density of N_2O_4 at a certain temperature is 30. What is the % dissociation of N_2O_4 at this temperature ?

- (A) 53.3 % (B) 106.6 %
(C) 26.7 % (D) None

Sol.

36. The equilibrium constant K_p (in atm) for the reaction is 9 at 7 atm and 300 K.



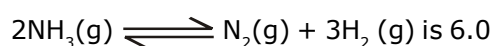
Calculate the average molar mass (in gm/mol) of an equilibrium mixture.

Given : Molar mass of A_2 , B_2 and C_2 are 70, 49 & 21 gm/mol respectively.

- (A) 50 (B) 45
(C) 40 (D) 37.5

Sol.

37. Vapour density of the equilibrium mixture of the reaction

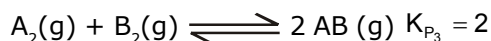
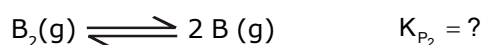
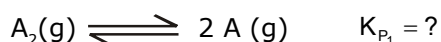


Percent dissociation of ammonia gas is :

- (A) 13.88 (B) 58.82
(C) 41.66 (D) None of these

Sol.

38. Equimolar mixture of two gases A_2 and B_2 is taken in a rigid vessel at temperature 300 K. The gases react according to given equations :



If the initial pressure in the container was 2 atm and final pressure developed at equilibrium is 2.75 atm.

in which equilibrium partial pressure of gas AB

was 0.5 atm, calculate the ratio of $\frac{K_{P_2}}{K_{P_1}}$.

[Given : Degree of dissociation of B_2 is greater than A_2].

- (A) 8 (B) 9
(C) 1/8 (D) None of these

Sol.

39. The heat of reaction at constant volume for an endothermic reaction in equilibrium is 1200 cal more than at constant pressure at 300K. Calculate the ratio of equilibrium constant K_p and K_c .

- (A) 1.648×10^{-3} (B) 1 : 1.
(C) 1 : 3 (D) 1 : 9

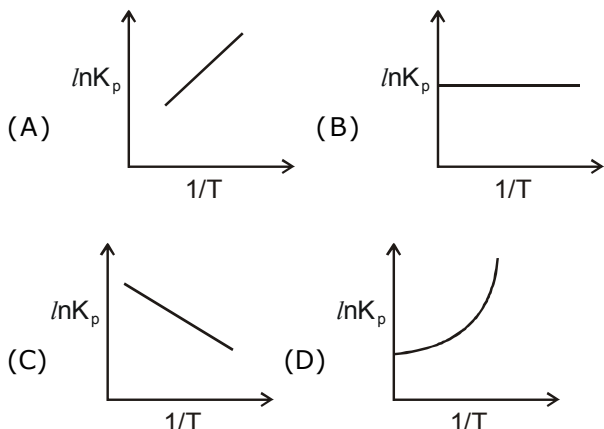
Sol.

40. When N_2O_5 is heated at temp. T , it dissociates as $N_2O_5 \rightleftharpoons N_2O_3 + O_2$, $K_c = 2.5$. At the same time N_2O_3 also decomposes as : $N_2O_3 \rightleftharpoons N_2O + O_2$. If initially 4.0 moles of N_2O_5 are taken in 1.0 litre flask and allowed to attain equilibrium, concentration of O_2 was found to be 2.5 M. Equilibrium concentration of N_2O is

- (A) 1.0 (B) 1.5
(C) 2.166 (D) 0.334

Sol.

41. An exothermic reaction is represented by the graph :



Sol.

42. A chemical reaction $A \rightleftharpoons B$ is said to be in equilibrium when -

- (A) Complete conversion of A to B has taken place
 (B) Conversion of A to B is only 50% complete
 (C) Only 10% conversion of A to B has taken place
 (D) The rate of transformation of A to B is just equal to rate of transformation of B to A in the system

Sol.

43. According to Law of Mass action, the rate of reaction is directly proportional to -

- (A) molarities of the reactants
 (B) normalities of the reactants
 (C) molalities of the reactants
 (D) mole fractions of the reactants

Sol.

44. In a chemical equilibrium, the equilibrium constant is found to be 2.5. If the rate constant of backward reaction is 3.2×10^{-2} , the rate constant of forward reaction is -

- (A) 8.0×10^{-2} (B) 4.0×10^{-2}
 (C) 3.5×10^{-2} (D) 7.6×10^{-3}

Sol.

45. K_1 and K_2 are the rate constants of forward and backward reactions. The equilibrium constant K of the reaction is -

- (A) $K_1 \times K_2$ (B) $K_1 - K_2$
 (C) $\frac{K_1}{K_2}$ (D) $\frac{K_1 + K_2}{K_1 - K_2}$

Sol.

46. The value of K_p for the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 50. What is the value of K_c

- (A) 30 (B) 40
 (C) 50 (D) 70

Sol.

47. For the reaction $A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$, the degree of dissociation α would be -

- (A) $\frac{\sqrt{K}}{\sqrt{K}+1}$ (B) $\sqrt{K} + 1$
 (C) $\sqrt{K} \pm 1$ (D) $\sqrt{K} - 1$

Sol.

48. An unknown compound A dissociates at 500°C to give products as follows -
 $A(g) \rightleftharpoons B(g) + C(g) + D(g)$
 Vapour density of the equilibrium mixture is 50 when it dissociates to the extent to 10%. What will be the molecular weight of Compound A -

- (A) 120 (B) 130
 (C) 134 (D) 140

Sol.

49. N_2O_4 dissociates as $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ at 273 K and 2 atm pressure. The equilibrium mixture has a density of 41. What will be the degree of dissociation -

- (A) 14.2% (B) 16.2%
 (C) 12.2% (D) None

Sol.

50. At 250°C and 1 atmospheric pressure, the vapour density of PCl_5 is 57.9. What will be the dissociation of PCl_5 -

- (A) 1.00 (B) 0.90
 (C) 0.80 (D) 0.65

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Which of the following statements is (are) correct ?
 (A) An irreversible reaction goes to almost completion.
 (B) a reversible reaction always goes to completion if carried out in a closed vessel
 (C) At equilibrium, the rate of forward reaction becomes equal to that of backward reaction.
 (D) In the beginning, the rate of backward reaction is much greater than that of forward reaction.

Sol.

2. The value of equilibrium constant of a reversible reaction at a given temperature :
 (A) depends on the initial concentration of reactants
 (B) depends on the concentration of products at equilibrium
 (C) gets reversed when the mode of representation of the reaction is reversed.
 (D) changes when the unit of active mass is changed.

Sol.

3. Which of the following statement is (are) correct ?
 (A) The value of equilibrium constant for a particular reaction is constant under all conditions of temperature and pressure.
 (B) The unit of K_c for the reaction.

$$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g) \text{ are mol L}^{-1}$$

 (C) In the reaction

$$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g).$$

$$[\text{CaCO}_3] = [\text{CaO}] = 1$$

 (D) K_p is always greater than K_c for a particular reaction.

Sol.

4. If it is found that the equilibrium constant increases by factor of four when the temperature is increased from 25°C to 40°C. The value of ΔH° is
 (A) 25.46 kJ (B) 171.65 kJ
 (C) 89.43 kJ (D) 71.65 kJ

Sol.

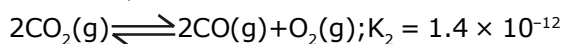
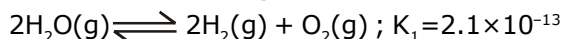
5. Ammonium carbamate dissociates as follows :

$$\text{NH}_2\text{COONH}_4(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)$$

 The value of K_p for this reaction is found to be equal to $2.92 \times 10^{-5} \text{ atm}^3$. If one mole of ammonium carbamate is heated in a sealed container, the total pressure developed in the container is
 (A) 0.0194 atm (B) 0.0388 atm
 (C) 0.0582 atm (D) 0.0667 atm

Sol.

6. The equilibrium constant for the following reactions at 1400 K are given.



Then, the equilibrium constant K for the reaction



- (A) 2.04 (B) 2.6
(C) 8.4 (D) 20.5

Sol.

7. Under what conditions of temperature and pressure, the formation of atomic hydrogen from molecular hydrogen will be favoured most ?

- (A) High temperature and high pressure
(B) Low temperature and low pressure
(C) High temperature and low pressure
(D) Low temperature and high pressure

Sol.

8. For the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$, the forward reaction at constant temperature is favoured by

- (A) introducing an inert gas at constant volume
(B) introducing chlorine gas at constant volume
(C) introducing an inert gas at constant pressure
(D) introducing PCl_5 at constant volume.

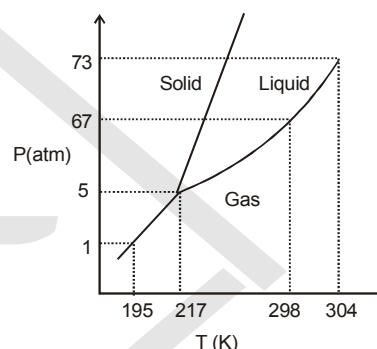
Sol.

9. When $\text{NaNO}_3(\text{s})$ is heated in a closed vessel, oxygen is liberated and $\text{NaNO}_2(\text{s})$ is left behind. At equilibrium.

- (A) addition of NaNO_2 favours reverse reaction
(B) addition of NaNO_3 favours forward reaction
(C) increasing temperature favours forward reaction
(D) increasing pressure favours reverse reaction

Sol.

10. Phase diagram of CO_2 is shown as following Based on above find the correct statement (s)



- (A) 298 K is the normal boiling point of liquid CO_2
(B) At 1 atm & 190 K CO_2 will exist as gas.
(C) $\text{CO}_2(\text{s})$ will sublime above 195 K under normal atmospheric pressure
(D) Melting point & boiling point of CO_2 will increase on increasing pressure.

Sol.

11. The equilibrium between, gaseous isomers A, B and C can be represented as

Reaction	Equilibrium constant
$A(g) \rightleftharpoons B(g)$: $K_1 = ?$
$B(g) \rightleftharpoons C(g)$: $K_2 = 0.4$
$C(g) \rightleftharpoons A(g)$: $K_3 = 0.6$

If one mole of A is taken in a closed vessel of volume 1 litre, then

- (A) $[A] + [B] + [C] = 1$ M at any time of the reactions.
 (B) Concentration of C is 4.1 M at the attainment equilibrium in all the reactions.

(C) The value of K_1 is $\frac{1}{0.24}$

- (D) Isomer [A] is least stable as per thermodynamics.

Sol.

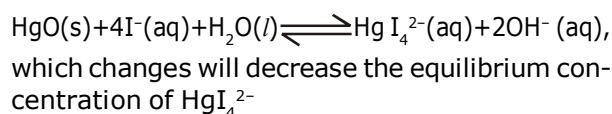
12. For the gas phase exothermic reaction.

$A_2 + B_2 \rightleftharpoons C_2$, carried out in a closed vessel, the equilibrium moles of A_2 can be increased by

- (A) increasing the temperature
 (B) decreasing the pressure
 (C) adding inert gas at constant pressure
 (D) removing some C_2

Sol.

13. Consider the equilibrium

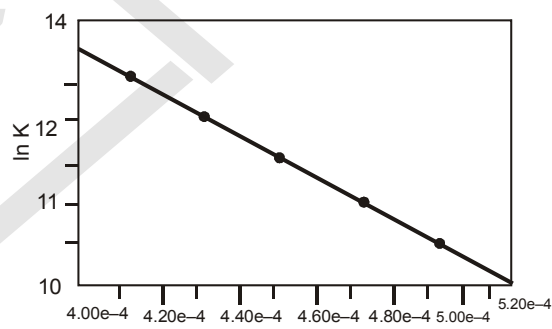


- (A) Addition of 0.1 M HI (aq)
 (B) Addition of HgO(s)
 (C) Addition of $H_2O(l)$
 (D) Addition of KOH (aq)

Sol.

14. In the laboratory the equilibrium constant for a particular reaction can be measured at different temperatures. Plotting the data yields the graph shown. Which of the following statements is false?

(Note : The notation 4.40 e- 4 is equivalent to 4.40×10^{-4})



- (A) ΔS° can be obtained from the y-intercept
 (B) The slope of the line is equal to $+\Delta H^\circ/R$
 (C) The reaction is endothermic
 (D) The standard free energy change of the reaction is positive.

Sol.

15. Decrease in the pressure for the following equilibria : $\text{H}_2\text{O (s)} \rightleftharpoons \text{H}_2\text{O (l)}$ result in the :
- (A) formation of more $\text{H}_2\text{O (s)}$
 (B) formation of more $\text{H}_2\text{O (l)}$
 (C) increase in melting point of $\text{H}_2\text{O (s)}$
 (D) decrease in melting point of $\text{H}_2\text{O (s)}$

Sol.

ASSERTION - REASON

In each sub-question below a statement S and an explanation E is given. Choose the correct answers from the codes A,B,C,D given for each question.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
 (C) Statement-1 is false, statement-2 is true.
 (D) Statement-1 is true, statement-2 is false.

16. **Statement-1** : Water boils at high temperature in pressure cooker.

Statement-2 : Increase in pressure leads to an increase in boiling point.

Sol.

17. **Statement-1** : A decrease in pressure leads to an increase in freezing point of water.

Statement-2 : For ice on melting volume decreases.

Sol.

18. **Statement-1** : The solubility of gases always increases with increase in pressure.

Statement-2 : High pressure favours the change where volume of gas decreases.

Sol.

19. **Statement-1** : Total number of moles in a closed system at new equilibrium is less than the old equilibrium if some amount of a substance is removed from a system.

$\text{A(g)} \rightleftharpoons \text{B(g)}$ equilibrium.

Statement-2 : The number of moles of the substance which is removed, is partially compensated as the system reached to new equilibrium.

Sol.

20. **Statement-1** : An exothermic reaction, non-spontaneous at high temperature, may become spontaneous at low temperature.

Statement-2 : Entropy of an exothermic reaction always decrease with decrease in temperature.

Sol.

- 21. Statement-1 :** Ammonia at a pressure of 10 atm and CO_2 at a pressure of 20 atm are introduced into an evacuated chamber. If K_p for the reaction.

$\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$ is 2020 atm^3 , the total pressure after a long time is less than 30 atm.

Statement-2 : Equilibrium can be attained from both directions.

Sol.

COMPREHENSION

Paragraph for Questions No. 22 to 25

In a 7.0 L evacuated chamber, 0.50 mol H_2 and 0.50 mol I_2 react at 427°C

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$. At the given temperature, $K_c = 49$ for the reaction.

- 22.** What is the value of K_p ?
 (A) 7 (B) 49
 (C) 24.5 (D) None

Sol.

- 23.** What is the total pressure (atm) in the chamber
 (A) 83.14 (B) 831.4
 (C) 8.21 (D) None

Sol.

- 24.** How many moles of the iodine remain unreacted at equilibrium ?

(A) 0.388 (B) 0.112
 (C) 0.25 (D) 0.125

Sol.

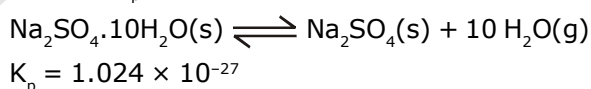
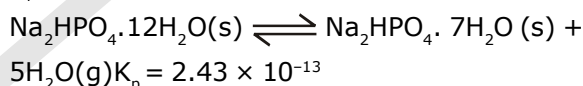
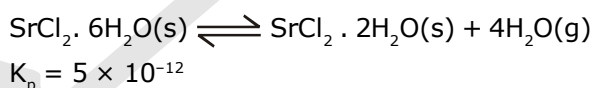
- 25.** What is the partial pressure (atm) of HI in the equilibrium mixture ?

(A) 6.385 (B) 12.77
 (C) 40.768 (D) 646.58

Sol.

Paragraph for Question Nos. 26 to 28

Equilibrium constants are given (in atm) for the following reactions at 0°C :



The vapour pressure of water at 0°C is 4.56 torr.

- 26.** Which is the most effective drying agent at 0°C ?

(A) $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ (B) $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$
 (C) Na_2SO_4 (D) all equally

Sol.

27. At what relative humidities will $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ be efflorescent (release moisture) when exposed to air at 0°C ?

(A) above 33.33 % (B) below 33.33 %
(C) above 66.66% (D) below 66.66%

Sol.

28. At what relative humidities will Na_2SO_4 be deliquescent (i.e. absorb moisture) when exposed to the air at 0°C ?

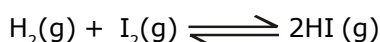
(A) above 33.33 % (B) below 33.33 %
(C) above 66.66% (D) below 66.66%

Sol.

Paragraph for Question Nos. 58 to 60

If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from the initial concentrations. Commonly only the initial concentration of reactants are given.

29. In a study of equilibrium



1 mole of H_2 and 3 mole of I_2 gave rise at equilibrium to x mol of HI.

Addition of a further 2 mol of H_2 gave an additional x mol of HI. What is x ?

(A) 0.5 (B) 1
(C) 1.5 (D) None of these

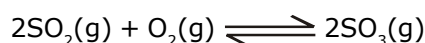
Sol.

30. In above problem, what is K_p at the temperature of the experiment.

(A) 1 (B) 2
(C) 4 (D) None of these

Sol.

31. In a study of equilibrium



Starting with 2 mole SO_2 and 1.5 mole O_2 in 5 litre flask. Equilibrium mixture required 0.4 mole KMnO_4 in acidic medium. Hence K_c is :

(A) 0.2 (B) 5.0
(C) 675.0 (D) None of these

Sol.

Match the column

32. Column I

- (A) $K_p < K_c$
(B) Introduction
(C) K_p^0 is dimensionless
(D) Temperature increase

Column II

- (P) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
(Q) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ of inert gas at pressure will decrease the constant concentration of reactants.
(R) $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
(S) $\text{NH}_3(\text{g}) + \text{HI}(\text{g}) \rightleftharpoons$ will shift the reaction $\text{NH}_4\text{I}(\text{s})$ on product side.

Sol.

33. Column-I

- (A) $A_{2(g)} + 3B_{2(g)} \rightleftharpoons 2AB_{3(g)}$
 (b) $A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$
 (C) $A_{(s)} + 1.5B_{2(g)} \rightleftharpoons 2AB_{3(g)}$
 (D) $AB_{2(g)} \rightleftharpoons AB_{(g)} + 0.5B_{2(g)}$

Sol.**Column-II K_p/K_c**

- (p) $(RT)^{-2}$
 (q) $(RT)^0$
 (r) $(RT)^{1/2}$
 (s) $(RT)^{-1/2}$

34. Column-I

- (A) $A_{2(g)} + B_{2(g)} \xrightleftharpoons{\text{Exothermic}} 2AB_{(g)}$
 (B) $2AB_{2(g)} + B_{2(g)} \xrightleftharpoons{\text{Exothermic}} 2AB_{3(g)}$
 (C) $2AB_{3(g)} \xrightleftharpoons{\text{Exothermic}} A_{2(g)} + 3B_{2(g)}$

Column-II factors affecting forward

- (p) High temperature
 (q) Low temperature
 (r) High pressure
 (s) Low pressure
 (t) Independent of pressure

INTEGER TYPE

- 35.** If a mixture of 3 mole of H_2 and 1 mole of N_2 is completely converted into NH_3 , what would be the final volume at same p and T?

Sol.

- 36.** For the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressure of CO_2 and CO are 2.0 atm and 4.0 atm respectively at equilibrium. Find the K_p for the reaction.

Sol.

- 37.** In the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the amounts of PCl_5 , PCl_3 and Cl_2 , 2 moles each at equilibrium and the total pressure is 3 atm. Find the equilibrium constant K_p .

Sol.

- 38.** For the equilibrium, $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$, K_p is 1.24×10^{-2} at $727^\circ C$. Find the value of K_c at $727^\circ C$.

Sol.

- 39.** The equilibrium constant for, $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$ is 0.469 atm at $1065^\circ C$ and heat of dissociation is 42.4 kcal. Calculate the equilibrium constant at $1132^\circ C$.

Sol.

- 40.** The molar concentration of A and B are 0.80 mol litre each. On mixing them, the reaction starts to proceed as : $A + B \rightleftharpoons C + D$, and attain equilibrium. At equilibrium molar concentration of C is 0.60 mol/litre. Find the value of K_c of the reaction.

Sol.

- 41.** In a reaction at equilibrium 'x' mole of the reactant A decompose to give 1 mole of C and D. It has been found that the fraction of A decomposed at equilibrium is independent of initial concentration of A. Find the value of x.

Sol.

42. In the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 6.75 atm. If 50% of CO_2 reacts, then find the value of K_p .

Sol.

43. N_2O_4 is 60% dissociated into NO_2 at 340K and 1 atm pressure. Find the volume of 10 g N_2O_4 occupy under these condition.

Sol.

44. Ammonium carbamate when heated to 473K gives a mixture of NH_3 and CO_2 vapour with a density of 13. Find the degree of dissociation of ammonium carbamate.

Sol.

45. In a experiment starting with 1 mole of C_2H_5OH , 1 mole of CH_3COOH and 1 mole of water, the equilibrium mixture on analysis shows that 54.3% of the acid is esterified. Find the value of K_c .

Sol.

46. Maximum number of phases at equilibrium of pure substance is

Sol.

47. The composition of the equilibrium mixture for the equilibrium $Cl_2 \rightleftharpoons 2Cl$ at 1470°K, may be determined by the rate of diffusion of mixture through a pin hole. It is found that at 1470°K, the mixture diffuses 1.16 times as fast as krypton (83.8) diffuses under the same conditions. Calculate the % degree of dissociation of Cl_2 at equilibrium.

Sol.

48. $2A(g) + B(g) \xrightleftharpoons{K_{eq}=2 \times 10^9} 3C(g)$

Initially only A & B are present in the container & moles of A and B at $t = 0$ are 4 & 2 respectively. If the concentration of A at equilibrium is $p \times 10^{-q}$ then find $p + q - 2$

Given : Volume of container is 100 lit.

Sol.

49. Ammonium carbamate dissociates as $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. In a closed vessel containing ammonium carbamate in equilibrium, ammonia is added such that partial pressure of NH_3 now equals to the original total pressure. Calculate the ratio of total pressure now to the original pressure as P/Q and give $P + Q$.

Sol.

50. In a study of the reaction $2A + 2B \rightleftharpoons 3C + D$, A and B are mixed in a vessel at $t^\circ C$. The initial conc. of A is twice the initial conc. of B. After equilibrium is reached, the conc of C is three times the conc. of B. Calculate the equilibrium constant K_c in terms of P/Q and report $P + Q$.

Sol.

EXERCISE – III**SUBJECTIVE PROBLEMS (JEE ADVANCED)****Reaction quotient and equilibrium constant**

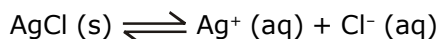
1. The initial concentrations or pressure of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the directions in which each system will shift to reach equilibrium.

- (a) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ $K = 17$
 $[\text{NH}_3] = 0.20 \text{ M}$; $[\text{N}_2] = 1.00 \text{ M}$; $[\text{H}_2] = 1.00 \text{ M}$
- (b) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ $K_p = 6.8 \times 10^4 \text{ atm}^2$
 Initial pressure : $\text{NH}_3 = 3.0 \text{ atm}$; $\text{N}_2 = 2.0 \text{ atm}$;
 $\text{H}_2 = 1.0 \text{ atm}$
- (c) $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ $K = 0.230 \text{ atm}$
 $[\text{SO}_3] = 0.00 \text{ M}$; $[\text{SO}_2] = 1.00 \text{ M}$; $[\text{O}_2] = 1.00 \text{ M}$
- (d) $2\text{SO}_3(\text{g}) \rightleftharpoons 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$ $K_p = 16.5 \text{ atm}$
 Initial pressure : $\text{SO}_3 = 1.0 \text{ atm}$; $\text{SO}_2 = 1.0 \text{ atm}$;
 $\text{O}_2 = 1.0 \text{ atm}$
- (e) $2\text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{NOCl}(\text{g})$ $K = 4.6 \times 10^4$
 $[\text{NO}] = 1.00 \text{ M}$; $[\text{Cl}_2] = 1.00 \text{ M}$; $[\text{NOCl}] = 0 \text{ M}$

Sol.

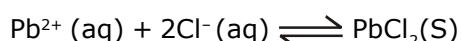
2. Among the solubility rules is the statement that all chlorides are soluble except Hg_2Cl_2 , AgCl , PbCl_2 and CuCl .

(a) Write the expression for the equilibrium constant for the reaction represented by the equation.



Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation

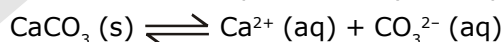


Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

Sol.

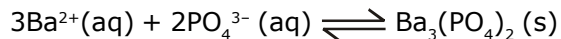
3. Among the solubility rules is the statement that carbonates, phosphates, borates, arsenates, and arsenites, except those of the ammonium ion and the alkali metals are insoluble.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation



Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by equation.



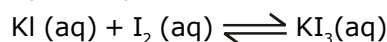
Is K greater than 1, less than 1, or about equal to 1? Explain your answer.

Sol.

4. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene. $3\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$
Would this reaction be most useful commercially if K were about 0.01, about 1, or about 10 ? Explain your answer.

Sol.

5. Show the complete chemical equation and the net ionic equation for the reaction represented by the equation

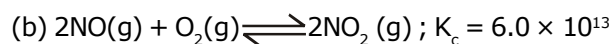


give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^- .

Sol.

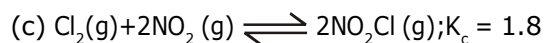
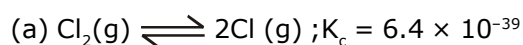
Using the equilibrium constant

6. Which of the following reactions goes almost all the way to completion, and which proceeds hardly at all ?



Sol.

7. For which of the following reactions will the equilibrium mixture contain an appreciable concentration of both reactants and products ?



Sol.

8. The value of K_c for the reaction

$3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$ is 1.7×10^{-56} at 25°C . Do you expect pure air at 25°C to contain much O_3 (ozone) when O_2 and O_3 are in equilibrium ? If the equilibrium concentration of O_2 in air at 25°C is $8 \times 10^{-3} \text{ M}$, what is the equilibrium concentration of O_3 ?

Sol.

9. At 1400 K, $K_c = 2.5 \times 10^{-3}$ for the reaction

$\text{CH}_4(\text{g}) + 2\text{H}_2\text{S} \rightleftharpoons \text{CS}_2(\text{g}) + 4\text{H}_2(\text{g})$. A 10.0 L reaction vessel at 1400 K contains 2.0 mol of CH_4 , 3.0 mol of CS_2 , 3.0 mol of H_2 and 4.0 mol of H_2S . Is the reaction mixture at equilibrium ? If not, in which direction does the reaction proceed to reach equilibrium ?

Sol.

10. The first step in the industrial synthesis of hydrogen is the reaction of steam and methane to give water gas, a mixture of carbon monoxide and hydrogen.

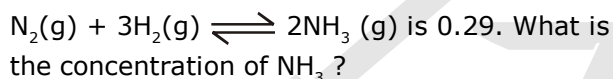


$$K_c = 4.7 \text{ at } 1400 \text{ K}$$

A mixture of reactants and product at 1400 K contains 0.035 M H_2O , 0.050 M CH_4 , 0.15 M CO , and 0.20 M H_2 . In which direction does the reaction proceed to reach equilibrium?

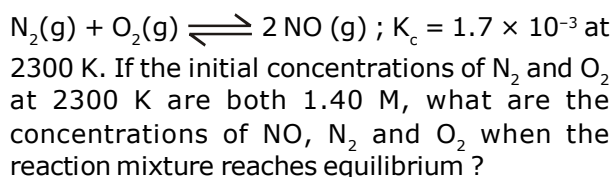
Sol.

11. An equilibrium mixture of N_2 , H_2 , and NH_3 at 700 K contains 0.036 M N_2 and 0.15 M H_2 . At this temperature, K_c for the reaction



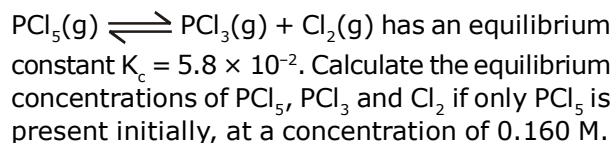
Sol.

12. The air pollutant NO is produced in automobile engines from the high temperature reaction



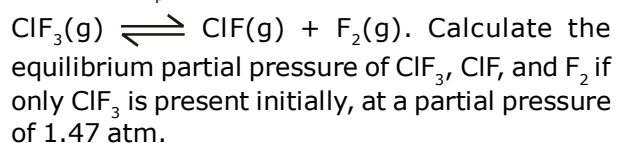
Sol.

13. At a certain temperature, the reaction



Sol.

14. At 700 K, $K_p = 0.140$ for the reaction



Homogeneous equilibria degree of dissociation, vapour density and equilibrium constant.

Sol.

15. The degree of dissociation of N_2O_4 into NO_2 at 1.5 atmospher and 40°C is 0.25. Calculate its K_p at 40°C . Also report degree of dissociation at 10 atmospheric pressure at same temperature.

Sol.

16. At 46° C K_p for the reaction

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.667 atm. Compute the percent dissociation of N_2O_4 at 46°C at a total pressure of 380 Torr.

Sol.

17. When 36.8 g $N_2O_4(g)$ is introduced into a 1.0-litre flask at 27°C. The following equilibrium reaction occurs :

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $K_p = 0.1642$ atm.

- Calculate K_c of the equilibrium reaction.
- What are the number of moles of N_2O_4 and NO_2 at equilibrium ?
- What is the total gas pressure in the flask at equilibrium ?
- What is the percent dissociation of N_2O_4 ?

Sol.

18. At some temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated, temperature remaining same.

Sol.

19. In a mixture of N_2 and H_2 in the ratio of 1 : 3 at 64 atmospheric pressure and 300°C, the percentage of ammonia under equilibrium is 33.33 by volume. Calculate the equilibrium constant of the reaction using the equation.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Sol.

20. The system $N_2O_4 \rightleftharpoons 2NO_2$ maintained in a closed vessel at 60° C & a pressure of 5 atm has an average (i.e. observed) molecular weight of 69, calculate K_p . At what pressure at the same temperature would the observed molecular weight be (230/3) ?

Sol.

21. The vapour density of N_2O_4 and NO_2 mixture at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Sol.

22. In the esterification

$\text{C}_2\text{H}_5\text{OH}(l) + \text{CH}_3\text{COOH}(l) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l)$
 an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant.

Sol.

Heterogeneous equilibrium

23. Solid Ammonium carbamate dissociates as :

$\text{NH}_2\text{COO NH}_4(s) \rightleftharpoons 2\text{NH}_3(g) + \text{CO}_2(g)$. In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium, ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure.

Sol.

24. A sample of $\text{CaCO}_3(s)$ is introduced into a sealed container of volume 0.821 litre & heated to 1000K until equilibrium is reached. The equilibrium constant for the reaction

$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ is 4×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.

Sol.

25. Anhydrous calcium chloride is often used as a desiccant. In the presence of excess of CaCl_2 , the amount of the water taken up is governed by $K_p = 6.4 \times 10^{85}$ for the following reaction at room temperature,

$\text{CaCl}_2(s) + 6\text{H}_2\text{O}(g) \rightleftharpoons \text{CaCl}_2 \cdot 6\text{H}_2\text{O}(s)$. What is the equilibrium vapour pressure of water in a closed vessel that contains $\text{CaCl}_2(s)$?

Sol.

26. 20.0 grams of $\text{CaCO}_3(s)$ were placed in a closed vessel, heated & maintained at 727°C under equilibrium $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ and it is found that 75% of CaCO_3 was decomposed. What is the value of K_p ? The volume of the container was 15 litres.

Sol.

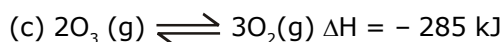
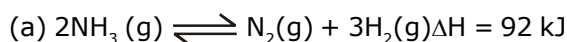
Changes in concentration at equilibrium Le Chatelier's principle

27. Suggest four ways in which the concentration of hydrazine, N_2H_4 , could be increased in an equilibrium described by the equation.

$\text{N}_2(g) + 2\text{H}_2(g) \rightleftharpoons \text{N}_2\text{H}_4(g) \quad \Delta H = 95 \text{ kJ}$

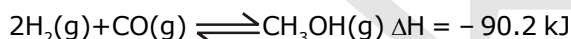
Sol.

28. How will an increase in temperature affect each of the following equilibria? An increase in pressure?



Sol.

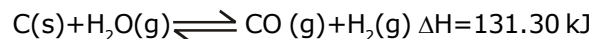
29. (a) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst. Write the expression for the equilibrium constant for the reversible reaction.



(b) Assume that equilibrium has been established and predict how the concentration of H_2 , CO and CH_3OH will differ at a new equilibrium if (i) more H_2 is added. (2) CO is removed. (3) CH_3OH is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased.. (6) more catalyst is added.

Sol.

30. (a) Water gas, a mixture of H_2 and CO , is an important industrial fuel produced by the reaction of steam with red-hot coke, essentially pure carbon, Write the expression for the equilibrium constant for the reversible reaction.



(b) Assume that equilibrium has been established and predict how the concentration of each reactant and product will differ at a new equilibrium if (1) more C is added. (2) H_2O is removed. (3) CO is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased.

Sol.

31. Ammonia is a weak base that reacts with water according to the equation

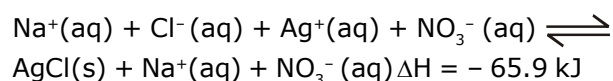


Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

- (a) Addition of NaOH . (b) Addition of HCl
(c) Addition of NH_4Cl .

Sol.

32. Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+ , Cl^- , Ag^+ and NO_3^- , in contact with solid AgCl .



Sol.

33. Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion in equilibrium with solid silver sulfate. Which of the following will occur ? (a) The Ag^+ and SO_4^{2-} concentration will not change. (b) The added silver sulfate will dissolve. (c) Additional silver sulfate will form and precipitate from solution as Ag^+ ions and SO_4^{2-} ions combine. (d) The Ag^+ ion concentration will increase and the SO_4^{2-} ion concentration will decrease.

Sol.

Kinetics and equilibrium constant

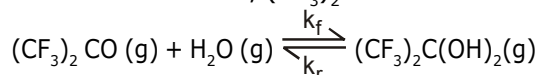
34. Consider a general, single-step reaction of the type $\text{A} + \text{B} \rightleftharpoons \text{C}$. Show that the equilibrium constant is equal to the ratio of the rate constant for the forward and reverse reaction, $K_c = \frac{k_f}{k_r}$.

Sol.

35. Which of the following relative values of k_f and k_r results in an equilibrium mixture that contains large amounts of reactants and small amounts of product ?
(a) $k_f > k_r$ (b) $k_f = k_r$ (c) $k_f < k_r$

Sol.

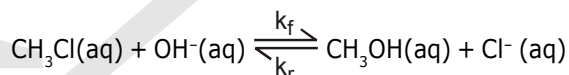
36. Consider the gas-phase hydration of hexafluoroacetone, $(\text{CF}_3)_2\text{CO}$:



At 76°C , the forward and reverse rate constants are $k_f = 0.13 \text{ M}^{-1} \text{ s}^{-1}$ and $k_r = 6.02 \times 10^{-4} \text{ s}^{-1}$. What is the value of the equilibrium constant K_c ?

Sol.

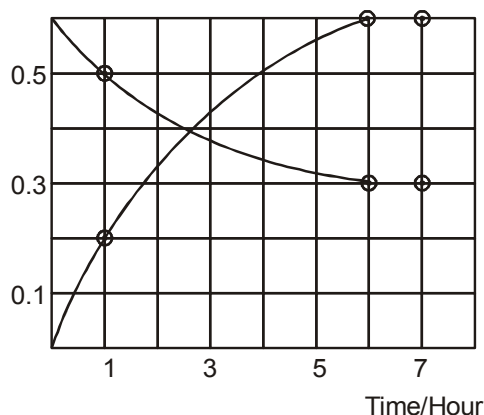
37. Consider the reaction of chloromethane with OH^- in aqueous solution



At 25°C , the rate constant for the forward reaction is $6 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$, and the equilibrium constant K_c is 1×10^{16} . Calculate the rate constant for the reverse reaction at 25°C .

Sol.

38. The progress of the reaction $A \rightleftharpoons nB$ with time, is presented in figure. Determine



- (i) the value of n .
 (ii) the equilibrium constant K .
 (iii) the initial rate of conversion of A .

Sol.

Temperature dependence of equilibrium constant

39. Listed in the table are forward and reverse rate constants for the reactions



Temperature (K)	$k_f (\text{M}^{-1}\text{s}^{-1})$	$k_r (\text{M}^{-1}\text{s}^{-1})$
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

Is the reaction endothermic or exothermic? Explain in terms of kinetics.

Sol.

40. Forward and reverse rate constant for the reaction $\text{CO}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{N}_2\text{O}$ exhibit the following temperature dependence.

Temperature (K)	$k_f (\text{M}^{-1}\text{s}^{-1})$	$k_r (\text{M}^{-1}\text{s}^{-1})$
1200	9.1×10^{-11}	1.5×10^5
1500	2.7×10^{-9}	2.6×10^5

Is the reaction endothermic or exothermic? Explain in terms of kinetics.

Sol.

41. The equilibrium constant K_p for the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ is 3.81×10^2 at 600 K and 2.69×10^3 at 700 K. Calculate $\Delta_r H$.

Sol.

Temperature dependence of equilibrium constant

42. Rate of disappearance of the reactant A at two different temperature is given by

$$A \rightleftharpoons B \quad \frac{-d[A]}{dt} = (2 \times 10^{-2} \text{ s}^{-1})[A] - 4 \times 10^{-3} \text{ s}^{-1} [B] ; 300 \text{ K}$$

$$\frac{-d[A]}{dt} = (4 \times 10^{-2} \text{ s}^{-1})[A] - 16 \times 10^{-4} [B] ; 400 \text{ K}$$

Calculate heat of reaction in the given temperature range. When equilibrium is set up.

Sol.

43. The K_p for reaction $A + B \rightleftharpoons C + D$ is 1.34 at 60°C and 6.64 at 100°C . Determine the standard free energy change of this reaction at each temperature and ΔH° for the reaction over this range of temperature ?

Sol.

46. A sample of HI (9.30×10^{-3} mol) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of I_2 was 6.29×10^{-4} M. Calculate the value of K_c at 1000 K for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$.

Sol.

Equilibrium expressions and equilibrium constants

44. If $K_c = 7.5 \times 10^{-9}$ at 1000 K for the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$, what is K_c at 1000 K for the reaction $2\text{NO}(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + \text{O}_2(\text{g})$?

Sol.

47. The vapour pressure of water at 25°C is 0.0313 atm. Calculate the values of K_p and K_c at 25°C for the equilibrium $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$.

Sol.

45. An equilibrium mixture of PCl_5 , PCl_3 and Cl_2 at a certain temperature contains 8.3×10^{-3} M PCl_5 , 1.5×10^{-2} M PCl_3 , and 3.2×10^{-2} M Cl_2 . Calculate the equilibrium constant K_c for the reaction $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$.

Sol.

EXERCISE – IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. For the reaction $\text{CO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}_2$, the

value of $\frac{K_p}{K_c}$ is - **[AIEEE-2002]**

- (A) $\frac{1}{RT}$ (B) \sqrt{RT}
 (C) $\frac{1}{\sqrt{RT}}$ (D) RT

Sol.

2. Which of the following equilibria is not affected by change in volume of the flask -

[AIEEE-2002]

- (A) $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 (B) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 (C) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$
 (D) $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$

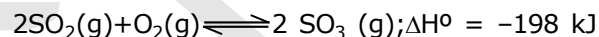
Sol.

3. For the reaction equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and $1.2 \times 10^{-2} \text{ mol L}^{-1}$ respectively. The value of K_c for the reaction is - **[AIEEE-2003]**

- (A) $3 \times 10^{-3} \text{ mol L}^{-1}$
 (B) $3 \times 10^3 \text{ mol L}^{-1}$
 (C) $3.3 \times 10^2 \text{ mol L}^{-1}$
 (D) $3 \times 10^{-1} \text{ mol L}^{-1}$

Sol.

4. Consider the reaction equilibrium



On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is - **[AIEEE-2003]**

- (A) Lowering the temperature and increasing the pressure
 (B) Any value of temperature and pressure
 (C) Lowering of temperature as well as pressure
 (D) Increasing temperature as well as pressure

Sol.

5. What is the equilibrium expression for the reaction $\text{P}_{4(\text{s})} + 5\text{O}_{2(\text{g})} \rightleftharpoons \text{P}_4\text{O}_{10(\text{s})}$?

[AIEEE-2004]

- (A) $K_c = [\text{P}_4\text{O}_{10}] / [\text{P}_4] [\text{O}_2]^5$
 (B) $K_c = [\text{P}_4\text{O}_{10}] / 5 [\text{P}_4] [\text{O}_2]$
 (C) $K_c = [\text{O}_2]^5$
 (D) $K_c = 1 / [\text{O}_2]^5$

Sol.

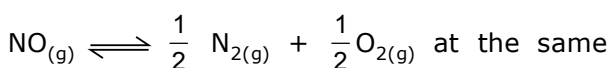
6. For the reaction $\text{CO}_{(\text{g})} + \text{Cl}_{2(\text{g})} \rightleftharpoons \text{COCl}_{2(\text{g})}$ the K_p/K_c is equal to -

[AIEEE-2004]

- (A) $\frac{1}{RT}$ (B) RT
 (C) \sqrt{RT} (D) 1.0

Sol.

7. The equilibrium constant for the reaction $\text{N}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightleftharpoons 2\text{NO}_{(\text{g})}$ at temperature T is 4×10^{-4} . The value of K_c for the reaction

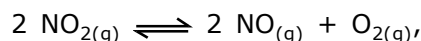


temperature is - [AIEEE-2004]

- (A) 2.5×10^2 (B) 50
 (C) 4×10^{-4} (D) 0.02

Sol.

8. For the reaction

 $(K_c = 1.8 \times 10^{-6} \text{ at } 184^\circ\text{C})$ $(R = 0.0831 \text{ kJ}/(\text{mol.K}))$

When K_p and K_c are compared at 184°C it is found that

[AIEEE-2005]

- (A) K_p is less than K_c
 (B) K_p is greater than K_c
 (C) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure
 (D) $K_p = K_c$

Sol.

9. The exothermic formation of ClF_3 is represented by the equation -



Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2 , F_2 and ClF_3 ?

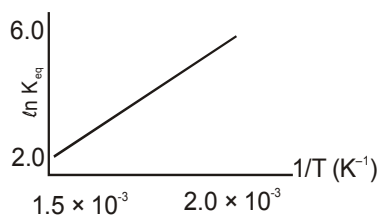
[AIEEE-2005]

- (A) Removing Cl_2
 (B) Increasing the temperature
 (C) Adding F_2
 (D) Increasing the volume of the container

Sol.

10. A schematic plot of $\ln K_{eq}$ versus inverse of temperature for a reaction is shown below

[AIEEE-2005]



The reaction must be

- (A) endothermic
(B) exothermic
(C) highly spontaneous at ordinary temperature
(D) one with negligible enthalpy change

Sol.

11. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for NH_4HS decomposition at this temperature is –

[AIEEE-2005]

- (A) 0.18 (B) 0.30
(C) 0.11 (D) 0.17

Sol.

12. Phosphorus pentachloride dissociates as follows, in a closed reaction vessel,



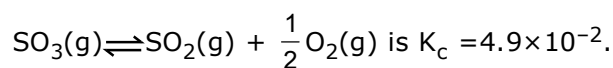
If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x , the partial pressure of PCl_3 will be

[AIEEE 2006]

- (A) $\left(\frac{2x}{1-x}\right)P$ (B) $\left(\frac{x}{x-1}\right)P$
(C) $\left(\frac{x}{1-x}\right)P$ (D) $\left(\frac{x}{x+1}\right)P$

Sol.

13. The equilibrium constant for the reaction



The value of K_c for the reaction
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ will be

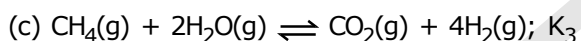
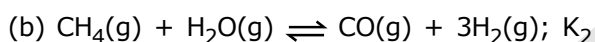
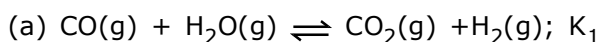
[AIEEE 2006]

- (A) 2.40×10^{-3} (B) 9.8×10^{-2}
(C) 4.9×10^{-2} (D) 416

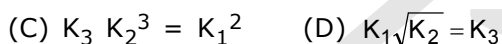
Sol.

14. For the following three reactions a, b and c, equilibrium constants are given

[AIEEE 2008]



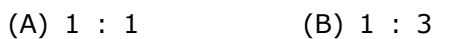
Which of the following relations is correct



Sol.

15. The equilibrium constants K_{p1} and K_{p2} for the reactions $\text{X} \rightleftharpoons 2\text{Y}$ and $\text{Z} \rightleftharpoons \text{P} + \text{Q}$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is -

[AIEEE 2008]



Sol.

16. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K_{p_i} :

[AIEEE 2011]



Sol.

17. The equilibrium constant (K_c) for the reaction $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)}$ at temperature T is 4×10^{-4} . The value of K_c for the reaction, $\text{NO(g)} \rightarrow \frac{1}{2} \text{N}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)}$ at the same temperature is:

[AIEEE 2012]



Sol.

LEVEL – II

JEE ADVANCED

1. The degree of dissociation is 0.4 at 400K & 1.0 atm for the gaseous reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2(\text{g})$. Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400K & 1.0 atm pressure. [JEE 1999]

Sol.

2. When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.
(i) Calculate K_c & K_p for the reaction at 27°C.
(ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask ? [JEE 2000]

Sol.

3. When two reactants A and B are mixed to give products C and D, the reaction quotient Q , at the initial stages of the reaction : [JEE 2000]
(A) is zero
(B) decrease with time
(C) independent of time
(D) increases with time

Sol.

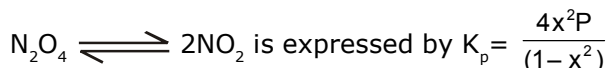
4. For the reversible reactions :
 $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 500°C. The value of K_p is 1.44×10^{-5} , when partial pressure is measured in atmospheres. The corresponding value of K_c with concentration in mol L^{-1} is :

- (A) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (B) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$
(C) $\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (D) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

[JEE 2000]

Sol.

6. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction.



where P is pressure, x is extent of decomposition.

Which of the following statement is true ?

- (A) K_p increases with increase of P
 (B) K_p increases with increases of x
 (C) K_p increases with the decrease of x
 (D) K_p remains constant with change in P or x

[JEE 2001]

Sol.

7. Consider the following equilibrium in a closed container : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$.

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α) :

- (A) Neither K_p nor α changes
 (B) Both K_p and α change
 (C) K_p changes, but α does not change
 (D) K_p does not change, but α changes

[JEE 2002]

Sol.

8. If $\text{Ag}^+ + \text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)]^+ ; K_1 = 1.6 \times 10^3$

and [JEE 2006]

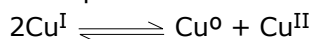


The formation constant of $[\text{Ag}(\text{NH}_3)_2]^+$ is :

- (A) 6.08×10^{-6} (B) 6.8×10^{-6}
 (C) 1.6×10^3 (D) 1.088×10^7

Sol.

9. The equilibrium



in aqueous medium at 25°C shifts towards the left in the presence of [JEE 2011]

- (A) NO_3^- (B) Cl^-
 (C) SCN^- (D) CN^-

Sol.

10. The thermal dissociation equilibrium of $\text{CaCO}_3(\text{s})$ is studied under different conditions.

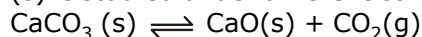


For this equilibrium, the correct statement(s) is (are) [JEE 2013]

- (A) ΔH is dependent on T
 (B) K is independent of the initial amount of CaCO_3
 (C) K is dependent on the pressure of CO_2 at a given T
 (D) ΔH is independent of the catalyst, if any

Sol.

11. The thermal dissociation equilibrium of $\text{CaCO}_3(\text{s})$ is studied under different conditions.



For this equilibrium, the correct statement(s) is (are)

- (A) ΔH is dependent on T
 (B) K is independent of the initial amount of CaCO_3
 (C) K is dependent on the pressure of CO_2 at a given T
 (D) ΔH is independent of the catalyst, if any

Answers

Answer Ex-I			OBJECTIVE PROBLEMS (JEE MAIN)										
1.	A	2.	A	3.	B	4.	A	5.	C	6.	B	7.	D
8.	A	9.	A	10.	B	11.	B	12.	D	13.	C	14.	A
15.	A	16.	D	17.	C	18.	B	19.	B	20.	B	21.	A
22.	A	23.	A	24.	C	25.	B	26.	D	27.	A	28.	A
29.	D	30.	C	31.	A	32.	B	33.	D	34.	A	35.	A
36.	C	37.	C	38.	A	39.	A	40.	D	41.	A	42.	D
43.	A	44.	A	45.	C	46.	C	47.	A	48.	A	49.	C
50.	C												

Answer Ex-II			OBJECTIVE PROBLEMS (JEE ADVANCED)										
1.	A,C	2.	C,D	3.	B	4.	D	5.	C	6.	B	7.	C
8.	C,D	9.	C,D	10.	C,D	11.	A,C,D	12.	A,B,C	13.	C,D	14.	B,D
15.	A,C	16.	A	17.	A	18.	A	19.	B	20.	C	21.	D
22.	B	23.	C	24.	B	25.	A	26.	A	27.	B	28.	A
29.	C	30.	C	31.	B	32.	(A) → P,R,S; (B) → P,Q,R,S; (C) → P,Q,R,S; (D) → Q						
33.	A→p; B→q; C→s; D→r					34.	A→p,t; B→q,r; C→q,s						
35.	2	36.	8	37.	1	38.	1	39.	1	40.	9	41.	2
42.	9	43.	5	44.	1	45.	4	46.	3	47.	14	48.	9
49.	58	50.	43										

Answer Ex-III		SUBJECTIVE PROBLEMS (JEE ADVANCED)	
1.	(a) 25, shifts left, (b) 0.22, shifts right, (c) ∞ , shifts left, (d) 1, shifts right, (e) 0, shift right		
2.	(a) $K = [\text{Ag}^+][\text{Cl}^-]$ is less than 1. AgCl is insoluble thus the concentration of ions are much less than 1 M		
	(b) $K = \frac{1}{[\text{Pb}^{2+}][\text{Cl}^-]^2}$ is greater than one because PbCl_2 is insoluble and formation of the solid will reduce the concentration of ions to a low level		
4.	K about 10	6. (a) incomplete (b) almost complete	7. c
		8. $\sim 9 \times 10^{-32}$ mol/L	
9.	The reaction is not an equilibrium because $Q_c > K_c$. The reaction will proceed from right to left to reach equilibrium		
11.	5.9×10^{-3} M	12. $[\text{NO}] = 0.056$ M, $[\text{N}_2] = [\text{O}_2] = 1.37$ M	13. $[\text{PCl}_3] = [\text{Cl}_2] = 0.071$ M, $[\text{PCl}_5] = 0.089$
14.	$P_{\text{ClF}} = P_{\text{F}_2} = 0.389$ atm, $P_{\text{ClF}_3} = 1.08$ atm	15. $K_p = 0.4$, $a \approx 0.1$	16. 50%
17.	(a) 6.667×10^{-3} mol L^{-1} ; (b) $n(\text{N}_2\text{O}_4) = 0.374$ mol; $n(\text{NO}_2) = 0.052$ mol; (c) 10.49 atm (d) 6.44 %		

18. 0.97 atm 19. $K_p = 1.3 \times 10^{-3} \text{ atm}^{-2}$ 20. $K_p = 2.5 \text{ atm}$, $P = 15 \text{ atm}$ 21. 53.33 %
22. $K = 4$ 23. $\frac{31}{27}$ 24. 22.4 mg 25. $P_{\text{H}_2\text{O}} = 5 \times 10^{-15} \text{ atm}$ 26. 0.821 atm
27. add N_2 , add H_2 , increase the pressure, heat the reaction
28. (a) shift right, shift left, (b) shift right, no effect, (c) shift left, shift left, (d) shift left, shift right
29. (a) $K = [\text{CH}_3\text{OH}] / [\text{H}_2]^2 [\text{CO}]$,
 (b) 1. $[\text{H}_2]$ increase, $[\text{CO}]$ decrease, $[\text{CH}_3\text{OH}]$ increase ; 2. $[\text{H}_2]$ increase, $[\text{CO}]$ decrease, $[\text{CH}_3\text{OH}]$ decrease ;
 3. $[\text{H}_2]$ increase, $[\text{CO}]$ increase, $[\text{CH}_3\text{OH}]$ increase ; 4. $[\text{H}_2]$ increase, $[\text{CO}]$ increase, $[\text{CH}_3\text{OH}]$ increase ;
 5. $[\text{H}_2]$ increase, $[\text{CO}]$ increase $[\text{CH}_3\text{OH}]$ decrease ; 6. no change
30. (a) $K = [\text{CO}] [\text{H}_2] / [\text{H}_2\text{O}]$;
 (b) in each of the following cases the mass of carbon will change, but its concentration (activity) will not change.
 1. $[\text{H}_2\text{O}]$ no change, $[\text{CO}]$ no change, $[\text{H}_2]$ no change ; 2. $[\text{H}_2\text{O}]$ decrease; $[\text{CO}]$ decrease, $[\text{H}_2]$ decrease ;
 3. $[\text{H}_2\text{O}]$ increase, $[\text{CO}]$ increase, $[\text{H}_2]$ decrease; 4. $[\text{H}_2\text{O}]$ increase, $[\text{CO}]$ increase. $[\text{H}_2]$ increase ; 5. $[\text{H}_2\text{O}]$ decrease, $[\text{CO}]$ increase, $[\text{H}_2]$ increase.
31. b 32. Add NaCl or some other salt that produces Cl^- in the solution. Cool the solution.
33. a 34. $k_f [\text{A}] [\text{B}] = k_r [\text{C}]$; $\frac{k_f}{k_r} = \frac{[\text{C}]}{[\text{A}][\text{B}]} = K_c$
36. 216
38. (i) 2, (ii) 1.2 mol/L ; (iii) 0.1 moles/hr
39. k_r increase more than k_f , this means that E_a (reverse) is greater than E_a (forward). The reaction is exothermic when E_a (reverse) > E_a (forward).
42. 16.06 kJ 43. -810 J/mol ; -5872 J/mol and 41.3 KJ/mol
44. 1.3×10^8 45. 0.058
46. 29.0 47. $K_p = 0.0313 \text{ atm}$, $K_c = 1.28 \times 10^{-3}$

Answer Ex-IV

PREVIOUS YEARS PROBLEMS

LEVEL – I

JEE MAIN

- | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| 1. C | 2. C | 3. A | 4. A | 5. D | 6. A | 7. B |
| 8. B | 9. C | 10. B | 11. C | 12. D | 13. D | 14. B |
| 15. D | 16. A | 17. B | | | | |

LEVEL – II

JEE ADVANCED

- | | |
|----------------------------|---|
| 1. 4.54 g dm ⁻³ | 2. (i) $K_c = 8.1 \times 10^{-5} \text{ mol}^2 \text{ L}^{-2}$; $K_p = 4.91 \times 10^{-2} \text{ atm}^2$ (ii) No effect ; |
| 3. D | 4. D 6. D 7. D |
| 8. D | 9. B,C,D 10. ABD 11. ABD |

CHEMICAL BONDING

KEY CONCEPTS

INTRODUCTION

A molecule will be formed if it is more stable and has a lower energy than the individual atom. Normally only electrons in the outermost shell of an atom are involved in forming bonds, and in this process each atom attains a stable electronic configuration of an inert gas.

Types of Bonds :

Atoms involved	Bonding
(I) Metal + Nonmetal	Ionic
(II) Nonmetal + Nonmetal	Covalent
(III) Metal + Metal	Metallic
(IV) Electron deficient molecule or ion (Lewis acid) and electron rich molecule or ion (Lewis base)	Coordinate
(V) H and electronegative elements (N, O, F some times with Cl)	Hydrogen

Ionic, Covalent and coordinate bonding

Ionic bonding

An ionic bond is formed when a metal atom transfers one or more electrons to a non-metal atom.



The oppositely charged ions get attracted through electrostatic force of attraction.

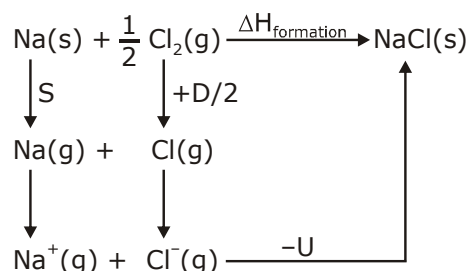
Properties of ionic compounds :

- In the solid state, each cation surrounds itself with anions and each anion with cations. These very large number of ions are arranged in an ordinary network called ionic crystals.
- They are good conductors of electricity in fused state or aqueous solution.
- They are generally soluble in polar solvents and insoluble in non-polar solvents.
- Have high melting point and boiling point than covalent compounds.
- Have strong force of attraction between cation and anion (Coulombic force)

$$F = \frac{Z_1 Z_2 e^2}{D r^2}$$

Where Z_1 and Z_2 are charge on the ions, D is dielectric constant of the medium and r the inner-ionic distance (i.e., bond length).

Born-Haber cycle It is an indirect method to calculate the lattice energy of an ionic compound. For example, the lattice energy of sodium chloride can be calculated as follows.



Now, according to Hess's law,

$$\Delta H_{\text{formation}} = S + IE_1 + D/2 - EA_1 - U$$

Where S is the enthalpy of sublimation of metal (Na), IE_1 is the first ionisation energy of sodium, D is the bond dissociation energy of Cl_2 molecule, EA_1 is the first electron affinity of Cl, U is the lattice energy of NaCl(s) and $\Delta H_{\text{formation}}$ is the enthalpy of formation of NaCl .

Covalent Bonding :

Whenever Chemical bond is formed by sharing of electrons then it is named as covalent bond.

Coordinate Bonding or Dative Bond :

Whenever covalent bond is formed by unequal sharing of a pair of electrons between a Lewis base and Lewis acid is called coordinate bond.

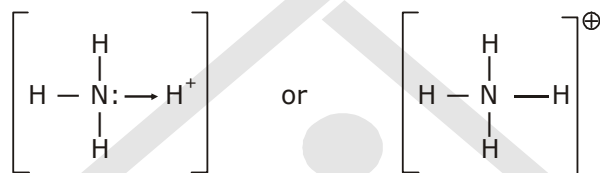
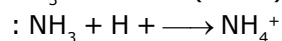
(I) It is represented as (\longrightarrow) and considered as σ bond.

(II) Atom/ion/molecule donating electron pair is called donor or Lewis base.

(III) Atom/ion/molecule accepting electron pair is called acceptor or Lewis acid.

Formation of NH_4^+ :

NH_3 has three (N – H) bonds and one lone pair. In NH_4^+ formation. This lone pair is donated to H^+ ion.



Note : In a multiple bond (\leftarrow) sign is treated as pi-covalent bond (Bock bond).

Valence Bond (V.B) theory :

According to this theory, a covalent bond is formed by the overlapping of atomic orbitals. Important points of this theory are summarised below.

(I) Orbitals undergoing overlapping should be half-filled.

(II) Half-filled orbitals should contain the electron with opposite spin.

(III) Strength of a covalent bond depends upon the extent of overlapping, for example, axial or lateral overlapping.

(IV) If the atomic orbitals overlap axially, then the bond formed is called a sigma (σ) bond.

(V) A sigma bond is always stronger than a pi-bond.

(VI) Covalent bonds formed by the overlap of s-s and s-p orbitals are always sigma.

(VII) By the overlap of p-p orbitals, one sigma and two pi bonds are formed.

(VIII) Increasing strength of σ covalent bonds is in the order $s - s < s - p < p - p$ (when internuclear distance is constant)

(IX) A single covalent bond is always a sigma bond. In a double covalent bond, one is sigma and the other is pi-bond. In a triple covalent bond, one is sigma and two are pi-bonds.

Hybridisation :

It is defined as the concept of intermixing of orbitals of same energy or of slightly different energy to produce entirely new orbitals of equivalent energy, identical shapes and which are symmetrically disposed in plane.

Important features of hybridisation are given below.

- (I) Only the orbitals generated are equal in number to that of pure atomic orbitals which are intermixed.
- (II) The hybrid orbitals generated are equal in number to that of pure atomic orbitals which are intermixed.
- (III) A hybrid orbital, like an atomic orbital, can have two electrons of opposite spins.
- (IV) Hybrid orbitals usually form sigma bonds. If there are pi-bonds, equal number of atomic orbitals must be left unhybridised for pi-bonding.

Valence shell electron pair repulsion (VSEPR) Theory (Gillespie theory) :

- (I) The shape of a molecule is determined by repulsion between the electron pairs (ℓp and bp) present in the valence shell of the central atom.
- (II) The order of repulsion is $(\ell p-\ell p) > (\ell p-bp) > (bp-bp)$

Determination of the Type of Hybridisation :

The number of electron pairs = Bond Pairs + Lone pairs
(σ Bond)

Table Shapes of molecules on the basis of VSEPR theory and hybridisation

Total electron pairs	Bond pairs	Lone pairs	Type of hybridization	Geometry due to repulsion	Bond angle	Example
2	2	0	sp	Linear	180°	$BeCl_2$
3	3	0	sp^2	Trigonal Planar	120°	BF_3
3	2	1	sp^2	Angular	$< 120^\circ$	SO_2
4	4	0	sp^3 or dsp^2	Tetrahedral	$109^\circ 28'$	CH_4
4	3	1	sp^3 or dsp^2	Pyramidal	$< 109^\circ 28'$	NH_3
4	2	2	sp^3 or sp^2	Bent	$< 109^\circ 28'$	H_2O
5	5	0	sp^3d	Trigonal bipyramidal	120° & 90°	PCl_5
5	4	1	sp^3d	See Saw	$< 120^\circ$ & $< 90^\circ$	SF_4
5	3	2	sp^3d	Bent T-shaped	$< 90^\circ$	ClF_3
5	2	3	sp^3d	Linear	180°	I_3^-
6	6	0	sp^3d^2	Octahedral	90°	SF_6
6	5	1	sp^3d^2	Square pyramidal	$< 90^\circ$	BrF_5
6	4	2	sp^3d^2	Square planar	90°	XeF_4
7	7	0	sp^3d^3	Pentagonal bipyramidal	90° & 72°	IF_7
7	6	1	sp^3d^3	Pentagonal pyramidal	$< 90^\circ$ & $< 72^\circ$	
7	5	2	sp^3d^3	Pentagonal planar	72°	XeF_5^-

Molecular Orbitals (M.O.) Theory :

- (I) There is Linear combination of Atomic Orbitals (LCAO) to form molecular orbitals (M.O.)

(II) The number of molecular orbitals produced is equal to the number of atomic orbitals that are combined.

(III) Two types of molecular orbitals are formed.

(a) Bonding molecular orbitals at a lower energy than the combining atomic orbitals which favour bond formation.

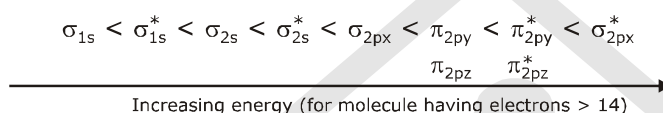
(b) Anti - bonding molecular orbitals at a higher energy than the combining atomic orbitals which opposes the bond formation.

Following molecular orbitals are formed when atomic orbitals overlap.

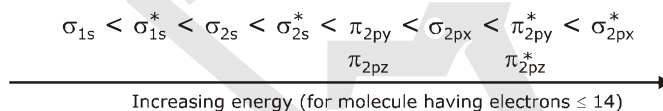
Atomic orbitals	Bonding M. O.	Anti-bonding M.O.
$1s + 1s$	$\sigma 1s$	$\sigma^* 1s$
$2s + 2s$	$\sigma 2s$	$\sigma^* 2s$
$2p_x + 2p_x$	$\sigma 2p_x$	$\sigma^* 2p_x$
$2p_y + 2p_y$	$\pi 2p_y$	$\pi^* 2p_y$
$2p_z + 2p_z$	$\pi 2p_z$	$\pi^* 2p_z$

Electrons are filled in the increasing order of energy of the molecular orbitals which is in order of Aufbau rule

(a) When total electrons in the molecule or ions are more than 14 (simple order of energy level of M. O.).



(b) When total number of electrons in the molecule are ions are ≤ 14 (modified order of energy level of M.O.).



(I) The electrons are filled in molecular orbitals in the same way as in atomic orbitals, that is, as per the Hund's Rule, Pauli exclusion principle and Aufbau rule.

(II) Number of covalent bonds between two atoms is called Bond order and is given by

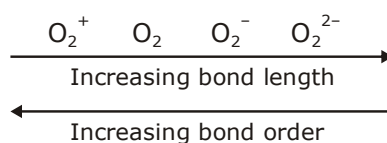
$$\text{Bond order (B.O.)} = \left(\frac{N_B - N_A}{2} \right)$$

Where, N_B = number of electrons in bonding molecular orbital and N_A = number of electrons in anti bonding molecular orbitals.

(III) For a stable molecule/ion, $N_B > N_A$

(IV) A given molecule or ion is paramagnetic if it has unpaired electrons in the molecular orbital. Otherwise it is diamagnetic

(V) Greater the bond order, shorter the bond length and greater the bond energy. Thus for O_2 , O_2^+ , O_2^- , O_2^{2-}



Fajan's Rule :

This rule is used to decide relative ionic & covalent character in a molecule. A molecule is predominantly covalent if

(I) Smaller the size of cation.

(II) larger the size of anion.

(III) greater the charge on cation and anion.

(IV) ion does not have inert gas configuration but it possesses pseudo inert gas configuration (18 electrons in the ultimate shell).

(I) $\xrightarrow{\text{LiCl} > \text{NaCl} > \text{KCl} > \text{RbCl} > \text{CsCl}}$
decreasing covalent character due to increase in the size of cation

(II) $\xrightarrow{\text{NaF} > \text{NaCl} > \text{NaBr} > \text{NaI}}$
decreasing ionic character because of increase in anionic size

(III) $\xrightarrow{\text{NaF} > \text{Na}_2\text{O} > \text{Na}_3\text{N}}$
increasing covalent nature due to increase of charge on anion and increase in size of anion

(IV) CuCl and NaCl

$[\text{Cu}^+] = [\text{Ar}]3d^{10}$; $[\text{Na}^+] = [\text{Ne}]$

Cations with 18-electron shells (pseudo inert gas configuration) has greater polarising power than 8-electron shell (inert gas configuration) ion with the same charge and size. Thus, CuCl is more covalent than NaCl.

Hydrogen Bonding :

(I) The concept of H-bonding was introduced by Latimer and Rodebush.

(II) H-bonding is said to be formed when slightly acidic hydrogen attached to a strongly electronegative atom such as F, O and N is held with weak electrostatic forces by the non-bonded pair of electron of another atom. That is, it is a dipole-dipole interaction.

(III) Of all the electronegative donor atoms, only F, O, and N enter into stable H-bond formation.

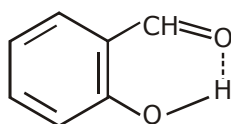
(IV) The weak electrostatic interaction leading to the H-bond formation is shown by dashed(.....) lines.

(V) Greater the electronegativity difference, stronger is the H-bond. For example,

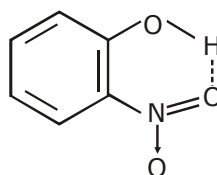
**Intramolecular H-bonding ;**

This type of H-bonding occurs when polar H and electronegative atom are present in the same molecule.

(a) o-hydroxy benzaldehyde



(b) o-nitrophenol

**Intermolecular H-bonding**

This type of H-bonding takes place between hydrogen and electronegative element (like F, O, N) present between molecules of the same substance (H_2O and H_2O) or different substances (H_2O and NH_3).

EXERCISE – I

OBJECTIVE PROBLEMS (JEE MAIN)

1. There is no S-S bond in

- (A) $S_2O_4^{2-}$ (B) $S_2O_5^{2-}$
(C) $S_2O_3^{2-}$ (D) $S_2O_7^{2-}$

Sol.

2. Which of the following molecules are expected to exhibit intermolecular H-bonding

- I. Acetic acid II. o-nitrophenol
III. m-nitrophenol IV. o-boric acid
(A) I, II, III (B) I, II, IV
(C) I, III, IV (D) II, III, IV

Sol.

3. In which of the dimerisation process, the achievement of the octet is not the driving force.

- (A) $2AlCl_3 \longrightarrow Al_2Cl_6$ (B) $BeCl_2 \longrightarrow BeCl_2(solid)$
(C) $2ICl_3 \longrightarrow I_2Cl_6$ (D) $2NO_2 \longrightarrow N_2O_4$

Sol.

4. A : tetracyanomethane B : Carbondioxide
C : Benzene D : 1, 3-buta-di-ene
Ratio of σ and π bond is in order:

- (A) $A = B < C < D$ (B) $A = B < D < C$
(C) $A=B=C=D$ (D) $C < D < A < B$

Sol.

5. Which of the following models best describes the bonding within a layer of the graphite structure ?

- (A) metallic bonding (B) ionic bonding
(C) non-metallic covalent bonding
(D) van der Waals force

Sol.

6. In ICl_4^- , the shape is square planar. The number of bond pair-lone pair repulsion at 90° are :

- (A) 6 (B) 8
(C) 12 (D) 4

Sol.

7. Arrange the following in order of decreasing N-O bond length : NO_2^+ , NO_2^- , NO_3^-

- (A) $NO_3^- > NO_2^+ > NO_2^-$ (B) $NO_3^- > NO_2^- > NO_2^+$
(C) $NO_2^+ > NO_3^- > NO_2^-$ (D) $NO_2^- > NO_3^- > NO_2^+$

Sol.

8. The molecule is not having 3c-2e bond.

- (A) BeH_2 (dimer) (B) $BeH_2(solid)$
(C) C_2H_6 (D) B_2H_6

Sol.

9. In which of the following molecules / ions all the bonds are not of equal length.

- (A) SiF_4 (B) SF_4
(C) XeF_4 (D) BH_4^-

Sol.

10. The critical temperature of water is higher than that of O_2 because the H_2O molecules has :

- (A) fewer electrons than O_2
(B) two covalent bonds
(C) V - shape
(D) dipole moment

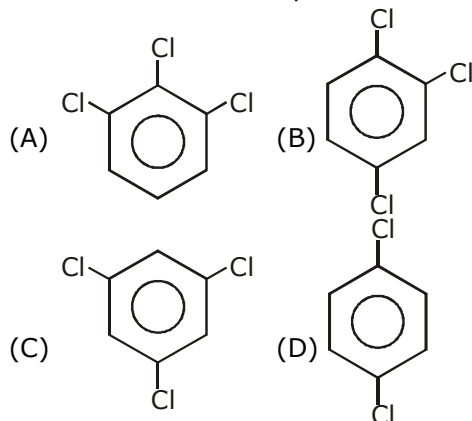
Sol.

11. Among KO_2 , AlO_2^- , BaO_2 and NO_2^+ unpaired electron is present in :

- (A) KO_2 only (B) NO_2^+ and BaO_2
(C) KO_2 and AlO_2^- (D) BaO_2 only

Sol.

12. Which has maximum dipole moment ?



Sol.

13. **Statement-1** : δ -bonds are formed by four lobes interaction of d-orbitals.**Statement-2** : d_{z^2} orbital does not have nodal plane.

- (A) Statement-1 is true , Statement-2 is true and Statement-2 is correct explanation for Statement-1
 (B) Statement-1 is true, Statement-2 is true and Statement-2 **NOT** the correct explanation for Statement-1
 (C) Statement-1 is true , Statement-2 is false
 (D) Statement-1 is false, statement-2 is true.

Sol.

14. Compound with maximum ionic character is formed from :

- (A) Na and Cl (B) Cs and F
 (C) Cs and I (D) Na and F

Sol.

15. Mg_2C_3 reacts with water forming propyne, C_3^{4-} has

- (A) two sigma and two pi bonds
 (B) three sigma and one pi bonds
 (C) two sigma and one pi bonds
 (D) two sigma and three pi bonds

Sol.

16. Which of the following has a geometry different from the other three species (having the same geometry)?

- (A) BF_4^- (B) SO_4^{2-}
 (C) XeF_4 (D) PH_4^+

Sol.

17. Which of the following molecule does not have open book structure.

- (A) O_2F_2 (B) H_2O_2
 (C) S_2Cl_2 (D) H_2C_2

Sol.

18. Among the following species, identify the isostructural pairs : NF_3 , NO_3^- , BF_3 , H_3O^+ , HN_3

- (A) $[NF_3, NO_3^-]$ and $[BF_3, H_3O^+]$
 (B) $[NF_3, HN_3]$ and $[NO_3^-, BF_3]$
 (C) $[NF_3, H_3O^+]$ and $[NO_3^-, BF_3]$
 (D) $[NF_3, H_3O^+]$ and $[HN_3, BF_3]$

Sol.

19. Number and type of bonds between two carbon atoms in CaC_2 are :

- (A) one sigma (σ) and one pi (π) bond
 (B) one σ and two π bonds
 (C) one σ and one and a half π bond
 (D) one σ bond

Sol.

20. C – C bond in C_2H_6 undergoes heterolytic fission, the hybridisation of two resulting carbon atoms is /are

- (A) sp^2 both (B) sp^3 both
 (C) sp^2 , sp^3 (D) sp , sp^2

Sol.

21. The hybridisation and geometry of BrF_3 molecules are :

- (A) sp^3d and T shaped (B) sp^2d^2 and tetragonal
(C) sp^3d and bent (D) none of these

Sol.

22. Pick out the incorrect statement ?

- (A) N_2 has greater dissociation energy than N_2^+
(B) O_2 has lower dissociation energy than O_2^+
(C) Bond length in N_2^+ is less than N_2
(D) Bond length in NO^+ is less than in NO .

Sol.

23. The correct order of increasing $\text{X} - \text{O} - \text{X}$ bond angle is ($\text{X} = \text{H}, \text{F}$ or Cl) :

- (A) $\text{H}_2\text{O} > \text{Cl}_2\text{O} > \text{F}_2\text{O}$ (B) $\text{Cl}_2\text{O} > \text{H}_2\text{O} > \text{F}_2\text{O}$
(C) $\text{F}_2\text{O} > \text{Cl}_2\text{O} > \text{H}_2\text{O}$ (D) $\text{F}_2\text{O} > \text{H}_2\text{O} > \text{Cl}_2\text{O}$

Sol.

24. Hybridization of carbon in C_3O_2 is :

- (A) sp (B) sp^2
(C) sp^3 (D) sp^3d

Sol.

25. Cyanogen, $(\text{CN})_2$, has a ___ shape/structure :

- (A) Linear (B) Zig-Zag
(C) Square (D) Cyclic

Sol.

26. Ethanol has a higher boiling point than dimethyl ether though they have the same molecular weight. This is due to :

- (A) resonance (B) coordinate bonding
(C) hydrogen bonding (D) ionic bonding

Sol.

27. Arrange the following in order of decreasing boiling point :

- (I) n-Butane (II) n-Butanol
(III) n-Butyl chloride (IV) Isobutane
(A) $\text{IV} > \text{III} > \text{II} > \text{I}$ (B) $\text{IV} > \text{II} > \text{III} > \text{I}$
(C) $\text{I} > \text{II} > \text{III} > \text{IV}$ (D) $\text{II} > \text{III} > \text{I} > \text{IV}$

Sol.

28. Which of the following compounds would have significant intermolecular hydrogen bonding ?

$\text{HF}, \text{CH}_3\text{OH}, \text{N}_2\text{O}_4, \text{CH}_4$

- (A) $\text{HF}, \text{N}_2\text{O}_4$ (B) $\text{HF}, \text{CH}_4, \text{CH}_3\text{OH}$
(C) $\text{HF}, \text{CH}_3\text{OH}$ (D) $\text{CH}_3\text{OH}, \text{CH}_4$

Sol.

29. For $\text{H}_2\text{O}_2, \text{H}_2\text{S}, \text{H}_2\text{O}$ and HF , the correct order of decreasing extent of hydrogen bonding is :

- (A) $\text{H}_2\text{O} > \text{HF} > \text{H}_2\text{O}_2 > \text{H}_2\text{S}$
(B) $\text{H}_2\text{O} > \text{HF} > \text{H}_2\text{S} > \text{H}_2\text{O}_2$
(C) $\text{HF} > \text{H}_2\text{O} > \text{H}_2\text{O}_2 > \text{H}_2\text{S}$
(D) $\text{H}_2\text{O}_2 > \text{H}_2\text{O} > \text{HF} > \text{H}_2\text{S}$

Sol.

30. A simplified application of MO theory to the hypothetical 'molecule' OF would give its bond order as

- (A) 2 (B) 1.5
(C) 1.0 (D) 0.5

Sol.

31. Which of the following contains electrovalent and covalent bonds ?

- (A) CH_4 (B) H_2O_2
(C) NH_4Cl (D) HCN

Sol.

32. Which of the following species is paramagnetic ?

- (A) NO^- (B) O_2^{2-}
(C) CN^- (D) CO

Sol.

33. Bond order of Be_2 is

- (A) 1 (B) 2
(C) 3 (D) 0

Sol.

34. The shape of methyl radical ($\dot{\text{C}}\text{H}_3$) is :

- (A) linear (B) pyramidal
(C) planar (D) spherical

Sol.

35. The structure of XeF_2 involves hybridization of the type :

- (A) sp^3 (B) dsp^2
(C) sp^3d (D) sp^3d^2

Sol.

36. NH_3 and BF_3 combine readily because of the formation of :

- (A) a covalent bond (B) a hydrogen bond
(C) a coordinate bond (D) an ionic bond

Sol.

37. The structure of diborane (B_2H_6) contains

- (A) Four ($2\text{C}-2\text{e}^-$) bonds and two ($2\text{C}-3\text{e}^-$) bonds
(B) Four ($2\text{C}-2\text{e}^-$) bonds and two ($3\text{C}-2\text{e}^-$) bonds
(C) Four ($2\text{C}-2\text{e}^-$) bonds and four ($3\text{C}-2\text{e}^-$) bonds
(D) None

Sol.

38. Which of the following equilibria would have the lowest value of K_p at a common temperature ?

- (A) $\text{MgCO}_3 \rightleftharpoons \text{MgO} + \text{CO}_2$
(B) $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$
(C) $\text{SrCO}_3 \rightleftharpoons \text{SrO} + \text{CO}_2$
(D) $\text{BaCO}_3 \rightleftharpoons \text{BaO} + \text{CO}_2$

Sol.

39. Which one of the following does not have inter-molecular H-bonding ?

- (A) H_2O (B) o-nitro phenol
(C) HF (D) CH_3COOH

Sol.

40. The order of strength of hydrogen bonds is :

- (A) $\text{ClH}\dots\text{Cl} > \text{NH}\dots\text{N} > \text{OH}\dots\text{O} > \text{FH}\dots\text{F}$
(B) $\text{ClH}\dots\text{Cl} < \text{NH}\dots\text{N} < \text{OH}\dots\text{O} < \text{FH}\dots\text{F}$
(C) $\text{ClH}\dots\text{Cl} < \text{NH}\dots\text{N} > \text{OH}\dots\text{O} > \text{FH}\dots\text{F}$
(D) $\text{ClH}\dots\text{Cl} < \text{NH}\dots\text{N} < \text{OH}\dots\text{O} > \text{FH}\dots\text{F}$

Sol.

41. The types of bond present in N_2O_5 are

- (A) only covalent (B) only ionic
(C) ionic and covalent (D) covalent & coordinate

Sol.

42. Which of the following exhibits/s H-bonding ?

- (A) CH_4 (B) H_2Se
(C) N_2H_4 (D) H_2S

Sol.

43. Select correct statement about hydrolysis of BCl_3 and NCl_3

- (A) NCl_3 is hydrolysed and gives HOCl but BCl_3 is not hydrolysed.
(B) Both NCl_3 and BCl_3 on hydrolysis gives HCl
(C) NCl_3 on hydrolysis gives HOCl but BCl_3 gives HCl .
(D) Both NCl_3 and BCl_3 on hydrolysis gives HOCl .

Sol.

44. The state of hybridisation for the transition state of hydrolysis mechanism of BCl_3 and SF_4 are respectively

- (A) sp^2 , sp^3d (B) sp^3 , sp^3
(C) sp^3 , sp^3d^2 (D) sp^3 , sp^3d

Sol.

45. The bond order depends on the number of electrons in the bonding and antibonding orbitals. Which of the following statement is / are correct about bond order ?

- (A) Bond order cannot have a negative value.
 (B) It always has an integral value
 (C) It is a nonzero quantity.
 (D) It can assume any value-positive or negative, integral or fractional, including zero.

Sol.

46. In the formation of N_2^+ from N_2 , the electron is removed from :

- (A) σ orbital (B) π orbital
 (C) σ^* orbital (D) π^* orbital

Sol.

47. The types of bonds present in $CuSO_4 \cdot 5H_2O$ are

- (A) electrovalent and covalent
 (B) electrovalent and coordinate covalent
 (C) covalent and coordinate covalent
 (D) electrovalent, covalent and coordinate covalent

Sol.

48. The polarizability of the following compounds is/are

- (A) $I^- > Br^- > Cl^- > F^-$ (B) $I^- > Br^- > F^- > Cl^-$
 (C) $I^- < Br^- < Cl^- < F^-$ (D) $I^- < Br^- < F^- < Cl^-$

Sol.

49. In the XeF_4 molecule, the Xe atom is in the

- (A) sp^2 -hybridized state
 (B) sp^3 -hybridised state
 (C) sp^2d -hybridized state
 (D) sp^3d^2 - hybridized state

Sol.

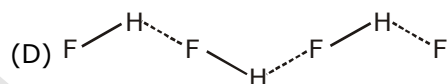
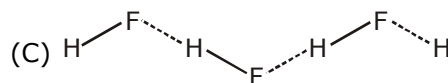
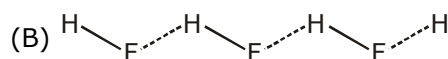
50. How many σ -and π -bonds are there in salicylic acid ?

- (A) $10\sigma, 4\pi$ (B) $16\sigma, 4\pi$
 (C) $18\sigma, 2\pi$ (D) $16\sigma, 2\pi$

Sol.

51. The bond in solid HF can be best represented as :

- (A) $H - F \dots H - F \dots H - F$

**Sol.**

52. For which of the following crystalline substances does the solubility in water increase upto $32^\circ C$ and then decrease rapidly ?

- (A) $CaCl_2 \cdot 2H_2O$ (B) $Na_2SO_4 \cdot 10H_2O$
 (C) $FeSO_4 \cdot 7H_2O$ (D) Alums

Sol.

53. Which of the following is true ?

- (A) Bond order $\propto \frac{1}{\text{bond length}} \propto \text{bond energy}$
 (B) Bond order $\propto \text{bond length} \propto \frac{1}{\text{bond energy}}$
 (C) Bond order $\propto \frac{1}{\text{bond length}} \propto \frac{1}{\text{bond energy}}$
 (D) Bond order $\propto \text{bond length} \propto \text{bond energy}$

Sol.

54. In which of the following processes magnetic moment and Bond order, both are changed.

- (A) $NO \longrightarrow NO^+$ (B) $O_2^+ \longrightarrow O_2$
 (C) $N_2 \longrightarrow N_2^-$ (D) All of these

Sol.

55. In which of the following cases, X-O bond length is not going to be changed (where X is the underline atom.)

- (A) H_3BO_3 taken in water
 (B) H_2SO_4 is taken in water
 (C) HNO_3 is taken in water
 (D) None of these

Sol.

56. Which of the following statement are not correct

- (A) Hybridization is the mixing of atomic orbitals
 (B) sp^2 - hybrid orbitals are formed from two p - atomic orbitals and one s - atomic orbitals
 (C) dsp^2 - hybrid orbitals are at 90° to one another
 (D) d^2sp^3 - hybrid orbitals are directed towards the corners of a regular octahedron

Sol.

57. Which of the following has been arranged in increasing order of size of the hybrid orbitals ?

- (A) $\text{sp} < \text{sp}^2 < \text{sp}^3$ (B) $\text{sp}^3 < \text{sp}^2 < \text{sp}$
 (C) $\text{sp}^2 < \text{sp}^3 < \text{sp}$ (D) $\text{sp}^2 < \text{sp} < \text{sp}^3$

Sol.

58. The shapes of PCl_4^+ , PCl_4^- and AsCl_5 are respectively

- (A) square planer, tetrahedral and see-saw
 (B) tetrahedral, see-saw and trigonal bipyramidal
 (C) tetrahedral, square planer and pentagonal bipyramidal
 (D) trigonal bipyramidal, tetrahedral and square pyramidal

Sol.

59. If a molecule MX_3 has zero dipole moment, the sigma bonding orbitals used by M (atm no. < 21) are

- (A) pure p (B) sp hybrid
 (C) sp^2 hybrid (D) sp^3 hybrid

Sol.

60. In the context of carbon, which of the following is arranged in the correct order of electronegativity

- (A) $\text{sp} > \text{sp}^2 > \text{sp}^3$ (B) $\text{sp}^3 > \text{sp}^2 > \text{sp}$
 (C) $\text{sp}^2 > \text{sp} > \text{sp}^3$ (D) $\text{sp}^3 > \text{sp} > \text{sp}^2$

Sol.

61. When 2s - 2s, 2p - 2p and 2p - 2s orbitals overlap, the bond strength decreases in the order :

- (A) $\text{p} - \text{p} > \text{s} - \text{s} > \text{p} - \text{s}$
 (B) $\text{p} - \text{p} > \text{p} - \text{s} > \text{s} - \text{s}$
 (C) $\text{s} - \text{s} > \text{p} - \text{p} > \text{p} - \text{s}$
 (D) $\text{s} - \text{s} > \text{p} - \text{s} > \text{p} - \text{p}$

Sol.

62. How many sigma and pi bonds are present in tetracyanoethylene ?

- (A) Nine σ and nine π (B) Five π and nine σ
 (C) Nine σ and Seven π (D) Eight σ and eight π

Sol.

63. The volatility of HF is low because of :

- (A) its low polarizability
 (B) the weak dispersion interaction between the molecules
 (C) its small molecular mass
 (D) its strong hydrogen bonding

Sol.

64. The shapes of IF_5 and IF_7 are respectively

- (A) tetragonal pyramidal and pentagonal bipyramidal
 (B) octahedral and pyramidal
 (C) trigonal bipyramidal and square antiprismatic
 (D) distorted square planer and distorted octahedral

Sol.

65. Which of the following has been arranged in order of decreasing dipole moment ?

- (A) $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$
 (B) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$
 (C) $\text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I} > \text{CH}_3\text{F}$
 (D) $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{I} > \text{CH}_3\text{Br}$

Sol.

66. Which of the following has the least dipole moment

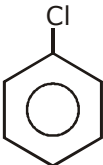
- (A) NF_3 (B) CO_2
 (C) SO_2 (D) NH_3

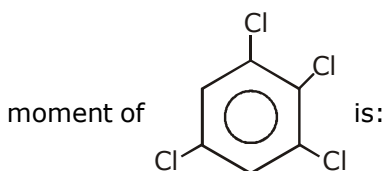
Sol.

67. The experimental value of the dipole moment of HCl is 1.03 D. The length of the H - Cl bonds is 1.275 Å. The percentage of ionic character in HCl is :

- (A) 43 (B) 21
 (C) 17 (D) 7

Sol.

68. The dipole moment of  is 1.5 D. The dipole



- (A) 0 D (B) 1.5 D
 (C) 2.86 D (D) 2.25 D

Sol.

69. Which of the following sets of characteristics leads to the increase in solubility of ionic substances ?

- (A) High dipole moment, Strong attraction by an ion and high solvation energy
 (B) Low dipole moment, weak attraction by an ion and high solvation energy
 (C) High dipole moment, Strong attraction by an ion and low solvation energy
 (D) High dipole moment, weak attraction by an ion and large solvation energy

Sol.

70. The correct order of increasing s-character (in percentage) in the hybrid orbitals of following molecules/ions is :

- (I) CO_3^{2-} (II) XeF_4 (III) I_3^-
 (IV) NCl_3 (V) BeCl_2
 (A) $\text{II} < \text{III} < \text{IV} < \text{I} < \text{V}$ (B) $\text{II} < \text{IV} < \text{III} < \text{V} < \text{I}$
 (C) $\text{III} < \text{II} < \text{I} < \text{V} < \text{IV}$ (D) $\text{II} < \text{IV} < \text{III} < \text{I} < \text{V}$

Sol.

71. Identify isostructural pairs from NF_3 (I), NO_3^- (II), BF_3 (III), H_3O^+ (IV), HN_3 (V)

- (A) I & II, III & IV (B) I & V, II & III
 (C) I & IV, II & III (D) I & IV, III & V

Sol.

72. The melting point of AlF_3 is 104°C and that of SiF_4 is -77°C (it sublimes) because :

- (A) there is very large difference in the ionic character of the Al - F and Si - F bonds
 (B) in AlF_3 , Al^{3+} interacts very strongly with the neighbouring F^- ions to give a three dimensional structure but in SiF_4 no such interaction is possible
 (C) the silicon ion in the tetrahedral SiF_4 is not shielded effectively from the fluoride ions whereas in AlF_3 , the Al^{3+} ion is shielded on all sides
 (D) The attractive forces between the SiF_4 molecules are strong whereas those between the AlF_3 molecules are weak

Sol.

73. Two ice cubes are pressed over each other and unite to form one cube. Which force is responsible for holding them together :

- (A) Vander Waal's forces
(B) Covalent attraction
(C) Hydrogen bond formation
(D) Dipole-dipole attraction

Sol.

74. Which of the following has fractional bond order :

- (A) O_2^{2+} (B) O_2^{2-}
(C) F_2^{2-} (D) H_2^-

Sol.

75. Carbon atoms in $C_2(CN)_4$ are :

- (A) sp -hybridized
(B) sp^2 -hybridized
(C) sp - and sp^2 hybridized
(D) sp , sp^2 and sp^3 -hybridized

Sol.

76. Molecular shapes of SF_4 , CF_4 and XeF_4 are :

- (A) the same, with 2, 0 and 1 lone pair of electrons respectively
(B) the same, with 1, 1 and 1 lone pair of electrons respectively
(C) different with 0, 1 and 2 lone pair of electrons respectively
(D) different with 1, 0 and 2 lone pair of electrons respectively

Sol.

77. Which has higher bond energy :

- (A) F_2 (B) Cl_2
(C) Br_2 (D) I_2

Sol.

78. In which of the following options, all bonds lengths are not equal

- (A) BF_3 (B) NF_3
(C) XeF_4 (D) ClF_3

Sol.

79. How many bonded electrons pairs are present in IF_7 molecule

- (A) 6 (B) 7
(C) 5 (D) 8

Sol.

80. In the cyanide ion the negative charge is on

- (A) C (B) N
(C) Both C and N
(D) Resonate between C and N

Sol.

81. The bond angle in PH_3 is :

- (A) Much lesser than NH_3
(B) Equal to that in NH_3
(C) Much greater than in NH_3
(D) Slightly more than in NH_3

Sol.

82. The ratio of σ and π bonds in benzene is

- (A) 2 (B) 6
(C) 4 (D) 8

Sol.

83. The hydration of ionic compounds involves :

- (A) Evolution of heat
- (B) Weakening of attractive forces of ions
- (C) Dissociation into ions
- (D) All of these

Sol.

84. H – B – H bond angle in BH_4^- is

- (A) 180°
- (B) 120°
- (C) 109°
- (D) 90°

Sol.

85. Which of the following species are hypervalent ?

1. ClO_4^- , 2. BF_3 3. SO_4^{2-} 4. CO_3^{2-}
- (A) 1, 2, 3
 - (B) 1, 3
 - (C) 3, 4
 - (D) 1, 2

Sol.

86. The bond angle and hybridization in ether (CH_3OCH_3) is :

- (A) $106^\circ 51'$, sp^3
- (B) $104^\circ 31'$, sp^3
- (C) 110° , sp^3
- (D) None of these

Sol.

87. In the series ethane, ethylene and acetylene, the C – H bond energy is

- (A) The same in all the three compounds
- (B) Greatest in ethane
- (C) Greatest in ethylene
- (D) Greatest in acetylene

Sol.

88. The enolic form of acetone contains :

- (A) 9 sigma, 1 pi bond and 2 lone pairs
- (B) 8 sigma, 2 pi bond and 2 lone pairs
- (C) 10 sigma, 1 pi bond and 1 lone pairs
- (D) 9 sigma, 2 pi bond and 1 lone pairs

Sol.

89. Type of hybridization in transition state of SeF_4 , when it undergoes in hydrolysis

- (A) sp^3d
- (B) sp^3d^2
- (C) dsp^3
- (D) sp^3

Sol.

90. Among LiCl , RbCl , BeCl_2 and MgCl_2 , the compounds with the greatest and the least ionic character respectively are :

- (A) LiCl and RbCl
- (B) RbCl and BeCl_2
- (C) RbCl and MgCl_2
- (D) MgCl_2 and BeCl_2

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. The total number of valence electrons in 4.2 g of N_3^- ion are :

(A) 2.2 N (B) 4.2 N
(C) 1.6 N (D) 3.2 N

Sol.

2. Oxidation state of 'S' in peroxodisulphuric acid and sodium tetrathionate

(A) +6, +5, 0 (B) +6, +6, +6
(C) +6, +4, +2 (D) +6, +2, +0

Sol.

3. How many unpaired electrons are present in N_2^+

(A) 1 (B) 2
(C) 3 (D) 4

Sol.

4. **Statement-1** : BeH_2 undergoes polymerisation while BH_3 undergoes dimerisation.

Statement-2 : Both are having incomplete octet under the polymerised and dimerised condition respectively.

(A) Statement-1 is true, Statement-2 is true and statement-2 is correct explanation for statement-1
(B) Statement-1 is true, Statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is true, Statement-2 is false.
(D) Statement-1 is false, Statement-2 is true.

Sol.

5. Intramolecular hydrogen bonding is found in

(A) Salicylaldehyde (B) Water
(C) Acetaldehyde (D) Phenol

Sol.

6. The pairs of bases in DNA are held together by
(A) Hydrogen bonds (B) Ionic bonds
(C) Phosphate groups (D) Deoxyribose group

Sol.

7. PCl_5 exists but NCl_5 does not because

(A) Nitrogen has no vacant d-orbital
(B) NCl_5 is unstable
(C) Nitrogen atom is much smaller than p
(D) Nitrogen is highly inert

Sol.

8. (C – Cl) bond in $CH_2=CH-Cl$ (vinyl chloride) is stabilized in the same ways as in

(A) benzyl chloride (B) ethyl chloride
(C) chlorobenzene (D) allyl chloride

Sol.

9. Which molecule is T shaped

(A) BeF_2 (B) BCl_3
(C) NH_3 (D) ClF_3

Sol.

10. Match list I with list II and select the correct answer :

List I (species)**List II (O – N – O angle)**

A. NO_2^+
B. NO_2
C. NO_2^-
D. NO_3^-

1. 180°
2. 134°
3. 120°
4. 115°
5. 109°

	A	B	C	D
(A)	5	4	3	2
(B)	5	2	4	3
(C)	1	2	4	3
(D)	1	4	3	2

Sol.

11. CO_2 is isostructural with :

- (A) HgCl_2 (B) SnCl_2 (C) C_2H_2 (D) NO_2

Sol.

12. The species/molecule is having same shape but different hybridisation.

- (A) XeF_2 , CO_2 (B) I_3^- , HgCl_2
(C) OCl^- , CO (D) SO_2 , OCl_2

Sol.

13. Which have fractional bond order ?

- (A) O_2^+ (B) O_2^- (C) NO (D) H_2^+

Sol.

14. Which has (have) zero value of dipole moment ?

- (A) I_2Cl_6 (B) CHCl_3
(C) CO_2 (D) $\text{Cl}-\text{C}_6\text{H}_4-\text{Cl}$

Sol.

15. Which of the following have planar structure ?

- (A) I_3^- (B) ICl_3
(C) Cl_2O_6 (D) Be_2Cl_4

Sol.

16. Which of the following have dipole moment ?

- (A) nitrobenzene (B) p-chloronitrobenzene
(C) m-dichlorobenzene (D) o-dichlorobenzene

Sol.

17. In the structure of H_2CSF_4 , which of the following statement is/are correct ?

- (A) Two C-H bonds are in the same plane of axial S-F bonds
(C) Two C-H bonds are in the same plane of equatorial S-F bonds
(C) Total six atoms are in the same plane
(D) Equatorial S-F plane is perpendicular to nodal plane of π -bond.

Sol.

18. Which of the following compounds contain(s) both ionic and covalent bonds ?

- (A) NH_4Cl (B) KCN
(C) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (D) NaOH

Sol.

19. Which of the following statements are **not correct**

- (A) All C-O bonds in CO_3^{2-} are equal but not in H_2CO_3 .
(B) All C-O bonds in HCO_2^- are equal but not in HCO_2H
(C) C-O bond length in HCO_2^- is longer than C-O bond length in CO_3^{2-} .
(D) C-O bond length in HCO_2^- and C-O bond length in CO_3^{2-} are equal.

Sol.

20. Resonance occurs due to the

- (A) delocalization of a lone pair of electrons
(B) delocalization of sigma electrons
(C) delocalization of pi electrons
(D) migration of protons

Sol.

21. Which of the following compounds possesses zero dipole moment ?

- (A) Water (B) Benzene
(C) Carbon tetrachloride (D) Boron trifluoride

Sol.

22. Which of the following compound is/are predominantly ionic?

- (A) KCl (B) Na₂S (C) H₂ (D) CaO

Sol.

23. Si₂O₇⁶⁻ anion is obtained when

- (A) no oxygen of a SiO₄ tetrahedron is shared with another SiO₄ tetrahedron.
(B) one oxygen of a SiO₄ tetrahedron is shared with another SiO₄ tetrahedron.
(C) two oxygen of a SiO₄ tetrahedron are shared with another SiO₄ tetrahedron.
(D) three or all four oxygens of a tetrahedron are shared with other SiO₄ tetrahedron.

Sol.

24. Which of the following statements is/are true?

- (A) Covalent bonds are directional
(B) Ionic bonds are nondirectional
(C) A polar bond is formed between two atoms which have the same electronegativity value.
(D) The presence of polar bonds in a polyatomic molecule suggests that it has zero dipole moment

Sol.

25. On heating to 400-500°C, relatively unstable hydrides and carbonates decompose. Which of the following will decompose when heated to 400-500°C

- (A) LiH (B) NaH (C) Li₂CO₃ (D) Na₂CO₃

Sol.

26. Which of the following have identical bond order?

- (A) O₂²⁺ (B) NO⁺ (C) CN⁻ (D) CN⁺

Sol.

27. Which of the following statement is/are correct

- (A) The peroxide ion has a bond order of 1 while the oxygen molecule has a bond order of 2
(B) The peroxide ion has a weaker bond than the dioxygen molecule has.
(C) The peroxide ion as well as the dioxygen molecules are paramagnetic
(D) The bond length of the peroxide ion is greater than that of the dioxygen molecule

Sol.

28. Given the species : N₂, CO, CN⁻ and NO⁺. Which of the following statements are true for these

- (A) All species are paramagnetic
(B) The species are isoelectronic
(C) All the species have dipole moment
(D) All the species are linear

Sol.

29. Which of the following have unpaired electron(s)

- (A) O₂⁺ (B) O₂⁻ (C) NO (D) H₂⁺

Sol.

30. Which of the following specie(s) is/are having only one corner shared per tetrahedron.

- (A) Si₂O₇⁶⁻ (B) Cr₂O₇²⁻
(C) S₂O₇²⁻ (D) Si₃O₉⁶⁻

Sol.

31. What is the state of hybridisation of Xe in cationic part of solid XeF_6

- (A) sp^3d^3 (B) sp^3d^2 (C) sp^3d (D) sp^3

Sol.

32. Rotation around the bond (between the underlined atoms) is restricted in :

- (A) C_2H_4 (B) H_2O_2 (C) C_2H_2 (D) C_2H_6

Sol.

33. According to MOT (Molecular Orbital Theory), the molecular orbitals are formed by mixing of atomic orbitals through LCAO (linear combination of atomic orbitals). The correct statement(s) about molecular orbitals is/are

Statement (A) : bonding molecular orbitals are formed by addition of wave-functions of atomic orbitals of same phase

Statement (B) : anti-bonding molecular orbitals are formed by subtraction of wave-functions of atomic orbitals of same phase

Statement (C) : non-bonding molecular orbitals do not take part in bond formation because they belong to inner shells

Statement (D) : anti-bonding molecular orbitals provide stability to molecules while bonding molecular orbitals make the molecules unstable.

- (A) Statement a, d (B) Statement a, b, c
(C) Statement a, b, d (D) Statement a, b

Sol.

34. NO X - X bond exists in which of the following compounds having general form of X_2H_6 ?

- (A) B_2H_6 (B) C_2H_6 (C) Al_2H_6 (D) Si_2H_6

Sol.

35. Which of the following species is (are) isostructural with XeF_4 ?

- (A) ICl_4^- (B) I_5^- (C) BrF_4^- (D) XeO_4

Sol.

36. In which of the following case central atom-F bond has partial double bond character?

- (A) NF_3 (B) CF_4 (C) PF_3 (D) OF_2

Sol.

37. Which one of the following compounds has bond angle as nearly 90° ?

- (A) NH_3 (B) H_2S (C) H_2O (D) SF_6

Sol.

38 The linear structure is assumed by :

- (A) SnCl_2 (B) NCO^- (C) CS_2 (D) NO_2^+

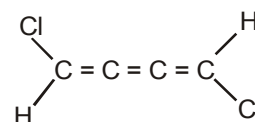
Sol.

39. Which of the following statements is/are correct?

- (A) NH_2^+ shows sp^2 - hybridisation whereas NH_2^- shows sp^3 - hybridisation
(B) $\text{Al}(\text{OH})_4^-$ has a regular tetrahedral geometry
(C) sp^2 - hybridized orbitals have equal s-and p-character
(D) Usually hybridized orbitals form σ - bonds

Sol.

40. Choose the correct option for the following molecule in view of chemical bonding



- (A) non-planar (B) $\mu \neq 0$
(C) A & B both (D) $\mu = 0$

Sol.

41. Of the following isoelectronic & isostructural species

are NO_3^- , ClO_3^- , SO_3 & CO_3^{2-}

- (A) NO_3^- & CO_3^{2-} (B) SO_3 & CO_3^{2-}
 (C) NO_3^- & ClO_3^- (D) CO_3^{2-} & ClO_3^-

Sol.

42. Shape of NH_3 is very similar to :

- (A) SeO_3^{2-} (B) CH_3^- (C) BH_3 (D) CH_3^+

Sol.

43. There is change in the type of hybridisation when

- (A) NH_3 combines with H^+
 (B) AlH_3 combines with H^-
 (C) NH_3 forms NH_2^- (D) SiF_4 forms SiF_6^{2-}

Sol.

44. Which of the following have same shape as NH_2^+ ?

- (A) CO_2 (B) SnCl_2 (C) SO_2 (D) BeCl_2

Sol.

45. Which of the following is (are) linear?

- (A) I_3^- (B) I_3^+ (C) PbCl_2 (D) XeF_2

Sol.

46. Which of the following statement is/are correct

- (A) Hybridisation is the mixing of pure atomic orbitals having less energy difference
 (B) $\text{sp}^3 \text{d}^2$ - hybrid orbitals are at 90° to one another
 (C) $\text{sp}^3 \text{d}$ - hybrid orbitals are directed towards the corners of a regular tetrahedron
 (D) $\text{sp}^3 \text{d}^2$ - hybrid orbitals are directed towards the corners of a regular octahedron

Sol.

47. Which of the following statements is/are true for BaO and MgO ?

- (A) BaO is more ionic than MgO
 (B) MgO is more ionic than BaO
 (C) BaO has a higher melting point than MgO
 (D) MgO has a higher melting point than BaO

Sol.

48. Polarization may be called the distortion of the shape of an anion by an adjacently placed cation. Which of the following statements is/are incorrect:

- (A) Minimum polarization is brought about by a cation of low radius
 (B) A large cation is likely to bring about a large degree of polarization
 (C) Maximum polarization is brought about by a cation of high charge
 (D) A small anion is likely to undergo a large degree of polarization

Sol.

49. Pick out among the following species isoelectronic with CO_2 :

- (A) N_3^- (B) $(\text{CNO})^-$ (C) $(\text{NCN})^{2-}$ (D) NO_2^-

Sol.

50. Which is correct statement?

As the s-character of a hybrid orbital decreases

- (I) The bond angle decreases
 (II) The bond strength increases
 (III) The bond length increases
 (IV) Size of orbital increases
 (A) (I), (III) and (IV) (B) (II), (III) and (IV)
 (C) (I) and (II) (D) All are correct

Sol.

51. Resonating structures of a molecule should have:

- (A) identical bonding
- (B) identical arrangement of atoms
- (C) nearly the same energy content
- (D) the same number of paired electrons

Sol.

52. Which of the following conditions apply to resonating structures ?

- (A) The contributing structures should have nearly similar energies
- (B) The contributing structures should be represented such that like charges reside on atoms that are far apart
- (C) The more electropositive element should preferably have positive charge and the more electronegative element have negative charge.
- (D) The contributing structures must have the same number of unpaired electrons

Sol.

53. A π -bond may form between two p_x orbitals containing one unpaired electron each when they approach each other appropriately along :

- (A) x-axis
- (B) y-axis
- (C) z - axis
- (D) any direction

Sol.

54. During the complete combustion of methane CH_4 , what change in hybridisation does the carbon atom undergo?

- (A) sp^3 to sp
- (B) sp^3 to sp^2
- (C) sp^2 to sp
- (D) sp^2 to sp^3

Sol.

55. The octet rule is not obeyed in :

- (A) CO_2
- (B) BCl_3
- (C) PCl_5
- (D) SiF_4

Sol.

56. N_2O has a linear, unsymmetrical structure that may be thought of as a hybrid of two resonance forms. If a resonance form must have a satisfactory Lewis structure, which two of the five structures shown below are the two resonance forms of N_2O ?

- (A) $:\text{N} \equiv \text{N} = \ddot{\text{O}}:$
- (B) $:\ddot{\text{N}} = \text{N} = \ddot{\text{O}}:$
- (C) $:\ddot{\text{N}} - \text{N} \equiv \text{O}:$
- (D) $:\ddot{\text{N}} = \ddot{\text{N}} - \ddot{\text{O}}:$
- (E) $:\text{N} \equiv \text{N} - \ddot{\text{O}}:$

Sol.

57. A, B, C are three substances. A does not conduct electricity in the solid, molten state and aqueous solution. B. Conducts electricity both in the fused and aqueous states, while C conducts electricity only in the aqueous state. In solid state neither B nor C conducts electricity. Which of the following statements is/are true regarding A, B and C ?

- (A) A has polar covalent linkage
- (B) A has nonpolar covalent linkage
- (C) B is ionic in nature
- (D) Cation formed by C is highly polarizing

Sol.

58. Three centre - two electron bonds exist in :

- (A) B_2H_6
- (B) $\text{Al}_2(\text{CH}_3)_6$
- (C) $\text{BeH}_2(\text{s})$
- (D) $\text{BeCl}_2(\text{s})$

Sol.

59. Which of the following statement(s) is/are correct regarding ionic compounds ?

- (A) They are good conductors of electricity at room temperature
 (B) They are always more soluble in polar solvents than covalent compounds
 (C) They consists of ions
 (D) They generally have high melting and boiling points

Sol.

60. Most ionic compounds have :

- (A) high melting points and low boiling points
 (B) high melting points and nondirectional bonds
 (C) high solubilities in polar solvents and low solubilities in nonpolar solvents
 (D) three-dimensional network structures, and are good conductors of electricity in the molten state.

Sol.

61. In which of the following cases, the number of lone pair on the central atom is two.

- (A) XeF_2 (B) XeF_4
 (C) ICl_2^+ (D) SO_2Cl_2

Sol.

62. Which of the following have a three dimensional network structure ?

- (A) SiO_2 (B) $(\text{BN})_x$
 (C) P_4 (white) (D) CCl_4

Sol.

63. To which of the following species octet rule is not applicable.

- (A) BrF_5 (B) SF_6 (C) IF_7 (D) CO

Sol.

64. Which of the following do not exist ?

- (A) SH_6 (B) HFO_4 (C) FeI_3 (D) HClO_3

Sol.

65. The species which contain an odd number of valence electrons and are paramagnetic :

- (A) NO (B) NO_2 (C) ClO_2 (D) N_2O_4

Sol.

66. Among the following, the element which show inert-pair effect are.

- (A) Bi (B) Sn
 (C) Pb (D) C

Sol.

67. Which of the following have an $(18 + 2)$ electron configuration ?

- (A) Pb^{2+} (B) Cd^{2+}
 (D) Bi^{3+} (D) SO_4^{2-}

Sol.

68. Which of the following pair of species is/are having same bond order and same magnetic moment.

- (A) He-H and H_2^- (B) O_2^+ and NO
 (C) He_2^+ and Li_2^+ (D) N_2^+ and N_2^-

Sol.

69. Which of the following oxyacids of sulphur contain S – S bonds ?

- (A) $\text{H}_2\text{S}_2\text{O}_8$ (B) $\text{H}_2\text{S}_2\text{O}_6$
 (C) $\text{H}_2\text{S}_2\text{O}_4$ (D) $\text{H}_2\text{S}_2\text{O}_5$

Sol.

70. Which of the following factors are responsible for origination of van der Waals forces?

- (A) Instantaneous dipole-induced dipole interaction
 (B) Dipole-induced dipole interaction and ion-induced dipole interaction
 (C) Dipole-dipole interaction and ion-induced dipole interaction
 (D) Small size of molecule

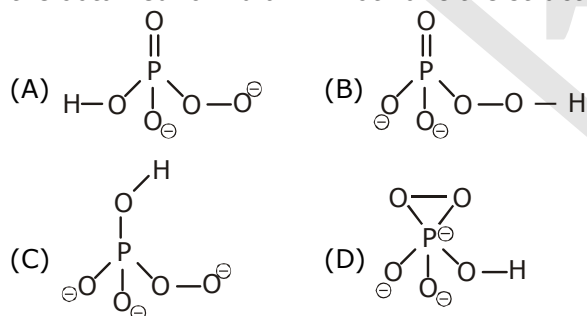
Sol.

71. Which of the following are true?

- (A) Van der Waals forces are responsible for the formation of molecular crystals
 (B) Branching lowers the boiling points of isomeric organic compounds due to decrease in vander Waals forces of attraction
 (C) In graphite, van der Waals forces act between the carbon layers
 (D) In diamond, van der Waals forces act between the carbon layers

Sol.

72. When H^+ is going to be added to the PO_5^{3-} , then the obtained formula will not have the structure of



Sol.

73. Intermolecular hydrogen bonding increases the enthalpy of vapourization of a liquid due to the:

- (A) decrease in the attraction between molecules
 (B) increase in the attraction between molecules
 (C) decrease in the molar mass of unassociated liquid molecules
 (D) increase in the effective molar mass of hydrogen-bonded molecules

Sol.

74. Which of the following molecules have intermolecular hydrogen bonds?

- (A) KH_2PO_4 (B) H_3BO_3
 (C) $C_6H_5CO_2H$ (D) CH_3OH

Sol.

75. Intramolecular hydrogen bonds occur in:

- (A) 2-chlorophenol
 (B) salicylic acid
 (C) the enol form of acetylacetone
 (D) paranitrophenol

Sol.

76. Which of the following are diamagnetic?

- (A) C_2 (B) O_2^{2-} (C) Li_2 (D) N_2^+

Sol.

77. Which of the following are paramagnetic?

- (A) B_2 (B) O_2 (C) N_2 (D) He_2

Sol.

78. Which of the following species have a bond order of 3?

- (A) CO (B) CN^- (C) NO^+ (D) O_2^+

Sol.

79. Among the following, the species with one unpaired electron are:

- (A) O_2^+ (B) NO (C) O_2^- (D) B_2

Sol.

80. Which of the following pairs have identical values of bond order?

- (A) N_2^+ and O_2^+ (B) F_2 and Ne_2
(C) O_2^{2-} and B_2 (D) C_2 and N_2

Sol.

81. Which of the following is correct ?

- (A) During N_2^+ formation, one electron is removed from the bonding molecular orbitals
(B) During O_2^+ formation, one electron is removed from the antibonding molecular orbitals.
(C) During O_2^- formation, one electron is added to the bonding molecular orbitals.
(D) During CN^- formation, one electron is added to the bonding molecular orbitals.

Sol.

82. Which of the following species are linear ?

- (A) ICl_2^- (B) I_3^- (C) N_3^- (D) ClO_2

Sol.

83. The structure of XeF_6 is :

- (A) pentagonal bipyramidal (B) distorted octahedral
(C) capped octahedral (D) square pyramidal

Sol.

84. sp^3 hybridisation is in :

- (A) AlH_4^- (B) CH_3^- (C) ClO_2^- (D) NH_2^-

Sol.

85. Choose the correct statements.

- (A) CH_3NCS molecule is linear
(B) SiH_3NCS molecule is linear
(C) GeH_3NCS molecule is bent
(D) $P(SiH_3)_3$ molecule is pyramidal

Sol.

Match the Column

86. Match the Column

Column-I

Column-II

- (A) I_2Cl_6 (P) All atoms are sp^3 hybridised
(B) SiC (Q) have non planar structure
(C) $Al_2(CH_3)_6$ (R) have 3c - 4e bonds
(D) S_3O_9 (S) have 3c - 2e bonds

Sol.

87. Match the Column

Column-I

Column-II

- (A) ICl_3 (P) Hybridisation of central atom is similar in both dimer and monomer form.
(B) $AlCl_3$ (Q) Both monomer and dimer forms are planar
(C) AlF_3 (R) In dimer form all atoms are sp^3 hybridised.
(D) NO_2 (S) Does not exist in dimer form

Sol.

88. Match the Column

Column-I

Column-II

- (Type of orbital) (Orbitals involved in hybridisation)
(A) d_{z^2} - orbital (P) sp^3 (Tetrahedral)
(B) s - orbital (Q) sp^3d^2 (Octahedral)
(C) $d_{x^2-y^2}$ (R) sp^3d (TBP)
(D) p_y - orbital (S) dsp^2 (square planar)

Sol.

COMPREHENSION TYPE QUESTIONS:

Passage-1

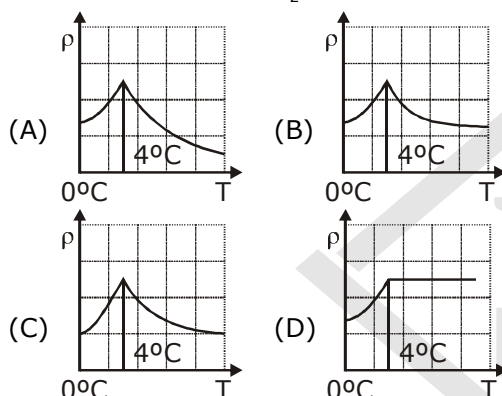
Hydrogen bonding originates from the dipole-dipole interaction between H-atom and any of the other atom like F, O, N and in some cases with Cl atom. There are two types of H-bonding like intermolecular and intramolecular H-bonding

89. Which of the following molecule does not consist of intramolecular H-bonding.

- (A) Chloral (B) Chloral hydrate
(C) ortho hydroxy benzaldehyde
(D) ortho chlorophenol

Sol.

90. Which of the following plot for ρ (density) v/s T (temperature) for liquid H_2O is correct.



Sol.

91. Which of following statement is incorrect

- (A) Boiling point of H_2O_2 is greater than that of H_2O
(B) Ethylene glycol is less viscous than glycerol.
(C) o-nitrophenol can be separated from its meta and para isomer using its steam volatile property.
(D) In ice each 'O' atom is tetrahedrally arranged by four H-atoms which are all equidistant.

Sol.

Passage-2

Phosphorus forms different halide compounds with halogens. In crystalline state some of them exist as ion pairs.

92. What is hybridisation of central atom of anionic part of PBr_5 in crystalline state.

- (A) sp^2 (B) sp^3 (C) sp (D) not applicable

Sol.

93. What is the difference between bond angles in cationic species of PCl_5 and PBr_5 in solid state.

- (A) 60° (B) $109^\circ 28'$ (C) 0° (D) 90°

Sol.

94. All possible bond angles in anionic part of PCl_5 are

- (A) $109^\circ 28'$ (B) $90^\circ, 180^\circ$
(C) $90^\circ, 120^\circ, 180^\circ$ (D) $72^\circ, 90^\circ, 180^\circ$

Sol.

Passage-3

Hybridisation is the mixing of atomic orbital of comparable energy and the number of hybrid orbitals formed is equal to the number of pure atomic orbitals mixed up and hybrid orbitals are occupied by σ -bond pair and lone pair.

95. Which of the following geometry is most likely to not form from sp^3d hybridisation of the central atom.

- (A) Linear (B) Tetrahedral
(C) T-Shaped (D) See-Saw

Sol.

96. The orbital is not participated in sp^3d^2 hybridisation.

- (A) p_x (B) d_{xy} (C) $d_{x^2-y^2}$ (D) p_z

Sol.

97. "The hybrid orbitals are at angle of X° to one another" this statement is not valid for which of the following hybridisation.

- (A) sp^3 (B) sp^2 (C) sp^3d^2 (D) sp

Sol.

EXERCISE – III**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. The geometry & the type of hybrid orbitals present about the central atom in BF_3 is :

- (A) linear, sp (B) trigonal planar, sp^2
(C) tetrahedral, sp^3 (D) pyramidal, sp^3

Sol.

2. The correct order of increasing C – O bond length of, CO , CO_3^{2-} , CO_2 is

- (A) $\text{CO}_3^{2-} < \text{CO}_2 < \text{CO}$ (B) $\text{CO}_2 < \text{CO}_3^{2-} < \text{CO}$
(C) $\text{CO} < \text{CO}_3^{2-} < \text{CO}_2$ (D) $\text{CO} < \text{CO}_2 < \text{CO}_3^{2-}$

Sol.

3. In the dichromate anion

- (A) 4 Cr-O bonds are equivalent
(B) 6 Cr-O bonds are equivalent
(C) all Cr-O bonds are equivalent
(D) all Cr-O bonds are non equivalent

Sol.

4. The geometry of H_2S and its dipole moment are :

- (A) angular & non zero (B) angular & zero
(C) linear & non zero (D) linear & zero

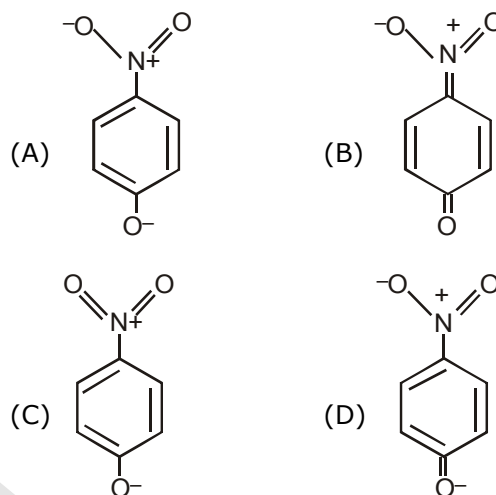
Sol.

5. In compounds type ECl_3 , where $\text{E} = \text{B}, \text{P}, \text{As}$ or Bi , the angles $\text{Cl} - \text{E} - \text{Cl}$ for different E are in the order

- (A) $\text{B} > \text{P} = \text{As} = \text{Bi}$ (B) $\text{B} > \text{P} > \text{As} > \text{Bi}$
(C) $\text{B} < \text{P} = \text{As} = \text{Bi}$ (D) $\text{B} < \text{P} < \text{As} < \text{Bi}$

Sol.

6. The most likely representation of resonance structure of p-nitrophenoxide is :



Sol.

7. Amongst H_2O , H_2S , H_2Se and H_2Te , the one with the highest boiling point is

- (A) H_2O because of hydrogen bonding
(B) H_2Te because of higher molecular weight
(C) H_2S because of hydrogen bonding
(D) H_2Se because of lower molecular weight

Sol.

8. The hybridization of atomic orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ are

- (A) sp^2 , sp^3 and sp^2 respectively
(B) sp , sp^2 and sp^3 respectively
(C) sp^2 , sp and sp^3 respectively
(D) sp^2 , sp^3 and sp respectively

Sol.

9. The correct order of hybridization of the central atom in the following species NH_3 , PtCl_4^{-2} , PCl_5 and BCl_3 is

- (A) dsp^2 , sp^3d , sp^2 and sp^3
 (B) sp^3 , dsp^2 , sp^3d , sp^2
 (C) dsp^2 , sp^2 , sp^3 , sp^3d
 (D) dsp^2 , sp^3 , sp^2 , sp^3d

Sol.

10. The common features among the species CN^- , CO and NO^+ are

- (A) Bond order three and isoelectronic
 (B) Bond order three and weak field ligands
 (C) Bond order two and π -acceptors
 (D) isoelectronic and weak field ligands

Sol.

11. Arrange the following species in decreasing order of bond angle. NO_2^+ , NO_2 , NO_2^-

Sol.

12. Find out the bond order of :

- (a) H_2 (b) H_2^+ (c) He_2
 (d) Li_2 (e) Be_2 (f) B_2

Sol.

13. Why does He_2^+ exist whereas He_2 does not ?

Sol.

14. Of the species O_2^+ , O_2^- , O_2 and O_2^{2-} which would have the maximum bond strength ?

Sol.

15. Write the electronic structures of :

(a) CO (b) NO (c) HF (d) HCl , based upon Molecular orbital (MO) diagram

Sol.

16. Of the following species which has the shortest bond length NO , NO^+ , NO^{2+} and NO^- ?

Sol.

17. Based upon M.O. theory state reason for the paramagnetic character of CN , the diamagnetic character of CN^- , the stability of CN^- and calculate their respective bond orders.

Sol.

18. In the hydrides of group 16th elements the bond angles decrease in the order, H_2O , H_2S , H_2Se , H_2Te . How would you account for this ?

Sol.

19. AgNO_3 gives a white precipitate with NaCl but not with CCl_4 . Why ?

Sol.

20. What should be the structure of the following as per VSEPR theory ?

- (a) XeF_2 (b) XeF_4 (c) PBr_5 (d) OF_2
 (e) I_3^- and (f) I_3^+

Sol.

21. In trimethylamine, the nitrogen has a pyramidal geometry whereas in trisilylamine $\text{N}(\text{SiH}_3)_3$ it has a planar geometry. Explain? Out of trimethylamine and trisilylamine which one is more basic and why ?

Sol.

22. The percent ionic character in HCl is 18.08. The observed dipole moment is 1.08 D. Find the inter nuclear distance in HCl.

Sol.

23. The dipole moment of LiH is 1.964×10^{-29} Cm and the intermolecular distance between Li and H in this molecule is 1.596 \AA . What is percent ionic character in molecule ?

Sol.

24. The dipole moment of KCl is 3.336×10^{-29} coulomb metre which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule, if these were opposite charges of one fundamental unit located at each nucleus. Calculate percentage ionic character of KCl.

Sol.

25. Assuming that all the four valency of carbon atom in propane pointing towards the corners of a regular tetrahedron. Calculate the distance between the terminal carbon atom in propane. Given, C – C single bond length is 1.54 \AA .

Sol.

26. Assuming covalent radii to be additive property; calculate the iodine-iodine distance in o^- , m^- , p^- di-iodobenzene. The benzene ring is regular hexagon and each C – I bond lies on a line passing through the centre of hexagon. The C – C bond length in C_6H_6 are 1.40 \AA and covalent radius of iodine and carbon atom are 1.33 \AA and 0.77 \AA . Also neglect different overlapping effect.

Sol.

27. The dipole moment of HBr is 7.95 debye and the interatomic separation is $1.94 \times 10^{-10} \text{ m}$. Find the % ionic character in HBr molecule.

Sol.

28. HBr has dipole moment 2.6×10^{-30} cm. If the ionic character of the bond is 11.5%, calculate the interatomic spacing.

Sol.

29. Dipole moment of LiF was experimentally determined and was found to be 6.32 D. Calculate percentage ionic character is LiF molecule Li-F bond length is 0.156 nm .

Sol.

30. A diatomic molecule has a dipole moment of 1.2 D. If bond length is 1.0 \AA , what percentage of an electronic charge exists on each atom.

Sol.

EXERCISE – IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. In which of the following species is the underlined carbon having sp^3 -hybridisation?

[AIEEE-2002]

- (A) $CH_3-\underline{C}OOH$ (B) $CH_3\underline{C}H_2OH$
(C) $CH_3\underline{C}OCH_3$ (D) $CH_2=\underline{C}H-CH_3$

Sol.

2. Which of the following statements is true?

[AIEEE-2002]

- (A) HF is less polar than HBr
(B) Water does not contain any ions
(C) Chemical bond formation takes place when forces of attraction overcome the forces of repulsion
(D) In covalent cond., transfer of electrons takes place

Sol.

3. A square planar complex is formed by hybridisation of which atomic orbital?

[AIEEE-2002]

- (A) s, p_x, p_y, d_{yz} (B) $s, p_x, p_y, d_{x^2-y^2}$
(C) s, p_x, p_y, d_{z^2} (D) s, p_x, p_y, d_{xy}

Sol.

4. The reason for double helical structure of DNA is operation of:

[AIEEE-2003]

- (A) dipole-dipole interaction
(B) hydrogen bonding
(C) electrostatic attraction
(D) vander Wall's forces

Sol.

5. Which one of the following pairs of molecules will have permanent dipole moments for both members:

[AIEEE-2003]

- (A) NO_2 and CO_2 (B) NO_2 and O_3
(C) SiF_4 and CO_2 (D) SiF_4 and NO_2

Sol.

6. The pair of species having identical shapes for molecules of both species is:

[AIEEE-2003]

- (A) XeF_2, CO_2 (B) BF_3, PCl_3
(C) PF_5, IF_5 (D) CF_4, SF_4

Sol.

7. The correct order of bond angles (smallest first) in H_2S, NH_3, BF_3 and SiH_4 is:

[AIEEE-2004]

- (A) $H_2S < NH_3 < SiH_4 < BF_3$
(B) $NH_3 < H_2S < SiH_4 < BF_3$
(C) $H_2S < SiH_4 < NH_3 < BF_3$
(D) $H_2S < NH_3 < BF_3 < SiH_4$

Sol.

8. The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for these two species?

[AIEEE-2004]

- (A) Bond length in NO^+ is equal to that in NO
(B) Bond length in NO is greater than in NO^+
(C) Bond length in NO^+ is greater than in NO
(D) Bond length is unpredictable

Sol.

9. The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are respectively: **[AIEEE-2004]**

(A) sp^3 and sp^2 (B) sp^2 and sp^3
(C) sp^2 and sp^2 (D) sp^3 and sp^3

Sol.

10. Which one of the following has the regular tetrahedral structure? **[AIEEE-2004]**

(A) BF_4^- (B) SF_4
(C) XeF_4 (D) $[\text{Ni}(\text{CN})_4]^{2-}$
(Atomic nos. : B = 5, S = 16, Ni = 28, Xe = 54)

Sol.

11. The maximum number of 90° angles between bond pair-bond pair of electrons is observed in: **[AIEEE-2004]**

(A) dsp^2
(B) sp^3d hybridization
(C) dsp^3 hybridization
(D) sp^3d^2 hybridization

Sol.

12. Beryllium and aluminium exhibit many properties which are similar. But, the two elements differ in: **[AIEEE-2004]**

(A) Forming covalent halides
(B) Forming polymeric hydrides
(C) Exhibiting maximum covalency in compound
(D) Exhibiting amphoteric nature in their oxides

Sol.

13. Which one of the following species is diamagnetic in nature? **[AIEEE-2005]**

(A) He_2^+ (B) H_2 (C) H_2^+ (D) H_2^-

Sol.

14. Lattice energy of an ionic compound depends upon: **[AIEEE-2005]**

(A) charge on the ion only
(B) size of the ion only
(C) packing of the ion only
(D) charge and size of the ion

Sol.

15. The molecular shapes of SF_4 , CF_4 and XeF_4 are: **[AIEEE-2005]**

(A) the same with 2, 0 and 1 lone pair of electrons on the central atom, respectively
(B) the same with 1, 1 and 1 lone pair of electrons on the central atoms, respectively
(C) different with 0, 1 and 2 lone pair of electrons on the central atoms, respectively
(D) different with 1, 0 and 2 lone pair of electrons on the central atoms, respectively

Sol.

16. Of the following sets which one does not contain isoelectronic species? **[AIEEE-2005]**

(A) PO_4^{3-} , SO_4^{2-} , ClO_4^- (B) CN^- , N_2 , C_2^{2-}
(C) SO_3^{2-} , CO_3^{2-} , NO_3^- (D) BO_3^{3-} , CO_3^{2-} , NO_3^-

Sol.

17. The number and type of bond between two carbon atom in calcium carbide are: **[AIEEE-2005]**

(A) One sigma, one pi bond
(B) One sigma, two pi bond
(C) Two sigma, one pi bond
(D) Two sigma, two pi bond

Sol.

18. Which of the following molecules\ions does not contain unpaired electrons?

[AIEEE-2006]

- (A) N_2^+ (B) O_2
(C) O_2^{2-} (D) B_2

Sol.

19. Among the following mixtures, dipole-dipole as the major interaction, is present in:

[AIEEE-2006]

- (A) KCl and water
(B) benzene and carbon tetrachloride
(C) benzene and ethanol
(D) acetonitrile and acetone

Sol.

20. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statements about these chlorides is correct?

[AIEEE-2006]

- (A) MCl_2 is more ionic than MCl_4
(B) MCl_2 is more easily hydrolysed than MCl_4
(C) MCl_2 is more volatile than MCl_4
(D) MCl_2 is more soluble in anhydrous ethanol than MCl_4

Sol.

21. In which of the following molecules/ions are all the bonds not equal? [AIEEE-2006]

- (A) XeF_4 (B) BF_4^- (C) SF_4 (D) SiF_4

Sol.

22. The decreasing value of bond angles from NH_3 (106°) to SbH_3 (101°) down group-15 of the periodic table is due to:

[AIEEE-2006]

- (A) decreasing lp – bp repulsion
(B) increasing electronegativity
(C) increasing bp – bp repulsion
(D) increasing p-orbital character in sp^3

Sol.

23. In which of the following ionization processes, the bond order has increased and the magnetic behaviour has changed

[AIEEE-2007]

- (A) $NO \rightarrow NO^+$ (B) $O_2 \rightarrow O_2^+$
(C) $N_2 \rightarrow N_2^+$ (D) $C_2 \rightarrow C_2^+$

Sol.

24. Which of the following hydrogen bonds is the strongest

[AIEEE-2007]

- (A) $F - H \cdots F$ (B) $O - H \cdots O$
(C) $O - H \cdots F$ (D) $O - H \cdots N$

Sol.

25. Which of the following species exhibits the diamagnetic behaviour: [AIEEE-2007]

- (A) O_2^+ (B) O_2
(C) NO (D) O_2^{2-}

Sol.

26. The charge/size ratio of a cation determines its polarizing power. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+ , Ca^{+2} , Mg^{+2} , Be^{+2}

[AIEEE-2007]

- (A) $Be^{+2} < K^+ < Ca^{+2} < Mg^{+2}$
(B) $K^+ < Ca^{+2} < Mg^{+2} < Be^{+2}$
(C) $Ca^{+2} < Mg^{+2} < Be^{+2} < K^+$
(D) $Mg^{+2} < Be^{+2} < K^+ < Ca^{+2}$

Sol.

27. Give reason carbon oxygen bond lengths in formic acid are 1.23 \AA & 1.36 \AA and both the carbon oxygen bonds in sodium formate have the same value i.e. 1.27 \AA

[JEE' 88]

Sol.

28. Explain why the dipole moment of NH_3 is more than that of NF_3 .

[JEE' 95]

Sol.

29. The experimentally determined N-F bond length in NF_3 is greater than the sum of single bond covalent radii of N & F. Explain.

[JEE'95]

Sol.

30. Explain the difference in the nature of bonding in LiF & LiI .

[JEE'96]

Sol.

31. Give reasons for the following in one or two sentences only.

[JEE'99]

- (a) BeCl_2 can be easily hydrolysed
(b) CrO_3 is an acid anhydride.

Sol.

32. Explain why o-hydroxybenzaldehyde is a liquid at room temperature, while p-hydroxybenzaldehyde is a high melting solid.

[JEE' 99]

Sol.

33. N_2 , O_2 , F_2 , Cl_2 in increasing order of bond dissociation energy.

[JEE' 88]

Sol.

34. Increasing strength of H-bonding. (X.....H-X)
O, S, F, Cl, N.

Sol.

35. Increasing order of extent of hydrolysis CCl_4 , MgCl_2 , AlCl_3 , PCl_5 , SiCl_4

Sol.

36. Arrange in increasing order of dipole moment.

[JEE'96]

- (I) Toluene, (II) m-dichlorobenzene
(III) O-dichlorobenzene (IV) P-dichlorobenzene.

Sol.

37. Arrange BeSO_4 , MgSO_4 , CaSO_4 , SrSO_4 in order of decreasing thermal stability.

[JEE'97]

Sol.

LEVEL – II

JEE ADVANCED

OBJECTIVE

1. Specify hybridization of N and B atoms in a 1 : 1 complex of BF_3 and NH_3 [JEE 2002]

- (A) N : tetrahedral, sp^3 ; B : tetrahedral, sp^3
 (B) N : pyramidal, sp^3 ; B: pyramidal, sp^3
 (C) N : pyramidal, sp^3 ; B : planar sp^2
 (D) N : pyramidal, sp^3 ; B : tetrahedral, sp^3

Sol.

2. The nodal plane in the π -bond of ethene is located in [JEE 2002]

- (A) the molecular plane
 (B) a plane parallel to the molecular plane
 (C) a plane perpendicular to the molecular plane which bisects, the carbon-carbon σ bond at right angle.
 (D) a plane perpendicular to the molecular plane which contains, the carbon-carbon bond.

Sol.

3. Identify the least stable ion amongst the following [JEE 2002]

- (A) Li^- (B) Be^- (C) B^- (D) C^-

Sol.

4. Which of the following molecular species has unpaired electron (s) ? [JEE 2002]

- (A) N_2 (B) F_2 (C) O_2^- (D) O_2^{2-}

Sol.

5. Which of the following are isoelectronic and isostructural ? NO_3^- , CO_3^{2-} , ClO_3^- , SO_3 [JEE 2003]

- (A) NO_3^- , CO_3^{2-} (B) SO_3 , NO_3^-
 (C) ClO_3^- , CO_3^{2-} (D) CO_3^{2-} , SO_3

Sol.

6. According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding O_2^+ [JEE 2004]

- (A) Paramagnetic and Bond order $< \text{O}_2$
 (B) Paramagnetic and Bond order $> \text{O}_2$
 (C) Diamagnetic and Bond order $< \text{O}_2$
 (D) Diamagnetic and Bond order $> \text{O}_2$

Sol.

7. Which species has the maximum number of lone pair of electrons on the central atom ? [JEE 2005]

- (A) ClO_3^- (B) XeF_4 (C) SF_4 (D) I_3^-

Sol.

8. The percentage of p-character in the orbitals forming P-P bonds in P_4 is [JEE 2007]

- (A) 25 (B) 33 (C) 50 (D) 75

Sol.

9. Among the following, the paramagnetic compound is [JEE 2007]

- (A) Na_2O_2 (B) O_3 (C) N_2O (D) KO_2

Sol.

10. The species having bond order different from that in CO is [JEE 2007]

- (A) NO^- (B) NO^+ (C) CN^- (D) N_2

Sol.

11. The structure of XeO_3 is [JEE 2007]

- (A) linear (B) planar (C) pyramidal (D) T-shaped

Sol.

12. Statement-1 : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.

Statement-2 : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. [JEE 2007]

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

Sol.

13. Statement-1 : In water, orthoboric acid behaves as a weak monobasic acid.

Statement-2 : In water, orthoboric acid acts as a proton donor. [JEE 2007]

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

Sol.

14. Statement-1 : Pb^{4+} compounds are stronger oxidizing agents than Sn^{4+} compounds. [JEE 2008]

Statement-2 : The higher oxidation states of group 14 elements are more stable for the heavier members of the group due to 'inert pair effect'.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

Sol.

15. Match each of the diatomic molecules in Column - I with its property/ properties in Column-II.

Column-I Column-II [JEE 2009]

- | | |
|---------------------------------|------------------------------------|
| (A) B ₂ | (P) Paramagnetic |
| (B) N ₂ | (Q) Undergoes oxidation |
| (C) O ₂ ⁻ | (R) Undergoes reduction |
| (D) O ₂ | (S) Bond order ≥ 2 |
| | (T) Mixing of 's' and 'p' orbitals |

Sol.

16. The nitrogen oxide(s) that contain(s) N-N bond(s) is (are).

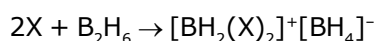
[JEE 2009]

- (A) N₂O (B) N₂O₃ (C) N₂O₄ (D) N₂O₅

Sol.

17. In the reaction

[JEE 2009]



the amine(s) X is (are) :

- (A) NH₃ (B) CH₃NH₂ (C) (CH₃)₂NH (D) (CH₃)₃N

Sol.

18. The species having pyramidal shape is

[JEE 2010]

- (A) SO₃ (B) BrF₃ (C) SiO₃²⁻ (D) OSF₂

Sol.

19. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B₂ is

[JEE 2010]

- (A) 1 and diamagnetic (B) 0 and diamagnetic
(C) 1 and paramagnetic (D) 0 and paramagnetic

Sol.

20. All the compounds listed in Column I react with water. Match the result of the respective reactions with the appropriate options listed in Column II.

Column-I Column-II [JEE 2010]

- | | |
|---|-------------------------------|
| (A) (CH ₃) ₂ SiCl ₂ | (P) Hydrogen halide formation |
| (B) XeF ₄ | (Q) Redox reaction |
| (C) Cl ₂ | (R) Reacts with glass |
| (D) VCl ₅ | (S) Polymerization |
| | (T) O ₂ formation |

Sol.

21. In Allen (C₃H₄), the type (s) of hybridisation of the carbon atoms is (are)

[JEE 2012]

- (A) sp and sp³ (B) sp and sp²
(C) only sp² (D) sp² and sp³

Sol.

22. The shape of XeO_2F_2 molecule is
 (A) trigonal bipyramidal [JEE 2012]
 (B) square planar
 (C) tetrahedral (D) see-saw

Sol.

23. With respect to graphite and diamond, which of the statement(s) given below is (are) correct? [JEE 2012]

- (A) Graphite is harder than diamond
 (B) Graphite has higher electrical conductivity than diamond.
 (C) Graphite has higher thermal conductivity than diamond.
 (D) Graphite has higher C – C bond order than diamond.

Sol.

Subjective

24. Decreasing order of the O–O bond length present in them O_2 , KO_2 and O_2 [AsF₄] [JEE 2004]

Sol.

25. The number of water molecule(s) directly bonded to the metal centre in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is [JEE 2009]

Sol.

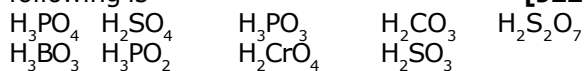
26. Based on VSEPR theory, the number of 90 degree F – Br – F angles in BrF_5 is [JEE 2010]

Sol.

27. The value of n in the molecular formula $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$ is [JEE 2010]

Sol.

28. The total number of diprotic acids among the following is [JEE 2010]



Sol.

29. Among the following, the number of elements showing only one non-zero oxidation state is : [JEE 2010]

O, Cl, F, N, P, Sn, Tl, Na, Ti

Sol.

30. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen [JEE 2012]

- (A) HNO_3 , NO, NH_4Cl , N_2
 (B) HNO_3 , NO, N_2 , NH_4Cl
 (C) HNO_3 , NH_4Cl , NO, N_2
 (D) NO, HNO_3 , NH_4Cl , N_2

Sol.

31. In Allene (C_3H_4), the type (s) of hybridisation of the carbon atoms is (are) [JEE 2012]

- (A) sp and sp^3 (B) sp and sp^2
 (C) only sp^2 (D) sp^2 and sp^3

Sol.

32. The shape of XeO_2F_2 molecule is [JEE 2012]

- (A) trigonal bipyramidal
 (B) square planar
 (C) tetrahedral
 (D) see-saw

Sol.

Answers

Answer Ex-I

OBJECTIVE PROBLEMS (JEE MAIN)

1. D	2. C	3. C	4. A	5. C	6. B	7. B	8. C	9. B	10. D
11. A	12. A	13. B	14. B	15. A	16. C	17. D	18. C	19. B	20. C
21. A	22. C	23. B	24. A	25. A	26. C	27. D	28. C	29. D	30. B
31. C	32. A	33. D	34. C	35. C	36. C	37. B	38. D	39. B	40. B
41. D	42. C	43. C	44. C	45. D	46. A	47. D	48. A	49. D	50. B
51. C	52. B	53. A	54. D	55. D	56. A	57. A	58. B	59. C	60. A
61. B	62. A	63. D	64. A	65. A	66. B	67. C	68. B	69. A	70. A
71. C	72. B	73. C	74. D	75. C	76. D	77. B	78. D	79. B	80. A
81. A	82. C	83. D	84. C	85. B	86. C	87. D	88. A	89. B	90. B

Answer Ex-II

OBJECTIVE PROBLEMS (JEE ADVANCED)

1. C	2. A	3. A	4. B	5. A
6. A	7. A	8. C	9. D	10. C
11. A, C	12. A, B, C, D	13. A, B, C, D	14. A, C, D	15. A, B, D
16. A, B, C, D	17. A, C, D	18. A, B, C, D	19. C, D	20. A, C
21. B, C, D	22. A, B, D	23. B	24. A, B	25. B, C
26. A, B, C	27. A, B, D	28. B, D	29. A, B, C, D	30. A, B, C
31. B	32. A, B, C	33. D	34. A, C	35. A, C
36. C	37. B, D	38. B, C, D	39. A, B, D	40. D
41. A	42. A, B	43. B, D	44. B, C	45. A, D
46. A, B, D	47. A, D	48. A, B, D	49. A, B, C	50. A
51. B, C, D	52. A, B, C, D	53. B, C	54. A	55. B, C
56. B, E	57. B, C, D	58. A, B, C	59. C, D	60. B, C, D
61. B, C	62. A, B	63. A, B, C	64. A, B, C	65. A, B, C
66. A, C	67. A, C	68. A, B, C, D	69. B, C, D	70. A, B, C
71. A, B, C	72. A, C, D	73. B, D	74. A, B, C, D	75. A, B, C
76. A, B, C	77. A, B	78. A, B, C	79. A, B, C	80. A, C
81. A, B, D	82. A, B, C	83. B, C	84. A, B, C, D	85. B, C, D

Match the column

86. A-R, B-P, C-S, D-Q	87. A-Q, B-R, C-S, D-P	88. A-QR, B-PQRS, C-QS, D-PQRS
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PASSAGE - 1

89. A	90. A	91. D
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PASSAGE - 2

92. D	93. C	94. B
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PASSAGE - 3

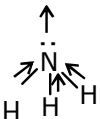


95. B	96. B	97. C
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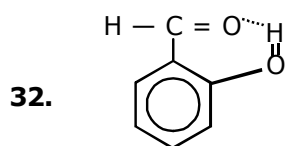
Answer Ex-III**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. B 2. D 3. B 4. A 5. B 6. A 7. A 8. B
 9. B 10. A
11.
$$\begin{array}{c} \oplus \\ \text{O} = \text{N} = \text{O} \\ \text{sp} \end{array}$$
 B.A. = 180° ,

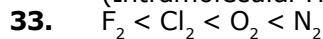
$$\text{O} = \text{N} = \text{O} \quad \text{sp}^2 \text{ bent}$$
 B.A. < 120° , \Rightarrow $\text{O} \leftarrow \overset{\bullet}{\text{N}} = \text{O} \quad \text{sp}^2$ B.A. = 120°
 $\text{NO}_2^+ > \text{NO}_2 > \text{NO}_2^-$
12. (a) H_2 B.O. = 1 (b) H_2^+ B.O. = 0.5 (c) He_2 B.O. = 0
 (d) Li_2 B.O. = 1 (e) Be_2 B.O. = 0 (f) B_2 B.O. = 1
13. He_2^+ B.O. = 0.5 He_2 B.O. = 0
14. O_2^+ 16. NO^+ 17. $2\frac{1}{2}, 3$ 23. 76.82% 24. 4.1652×10^{-29} coulomb metre
25. 2.514 Å 26. 3.50 Å, 6.06 Å, 7.0 Å 27. 85.32% 28. 1.4 Å 29. 84.35% 30. 25%

EXERCISE – IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

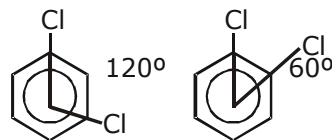
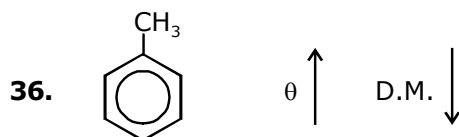
1. B 2. C 3. B 4. B 5. B 6. A 7. A
 8. B 9. B 10. A 11. D 12. C 13. B 14. D
 15. D 16. C 17. B 18. C 19. D 20. A 21. C
 22. D 23. A 24. A 25. D 26. B
27. As in $\text{HCOO}^- \text{Na}^+$
 \Rightarrow all resonating structure are equivalent \Rightarrow so all bond length will be equal.
28.  
29. 
30. Li F
 Li I
 According to Fajan $\text{I}^- > \text{F}^-$
 (polarisability)
 $\Rightarrow \text{Li F} > \text{Li I}$ (ionic character)
31. (i) Be has vacant orbital as electrophilic centre in it
 (ii) $\text{H}_2\text{CrO}_4 \rightleftharpoons \text{CrO}_3$
 Chromic acid chromic anhydride



(Intramolecular H-bond which reduces B.P.)



35.



IV < II < III < I



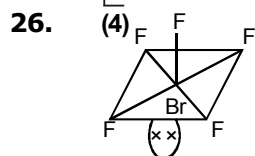
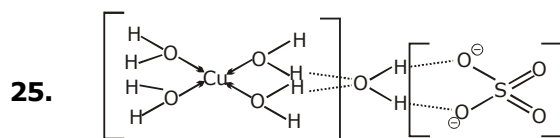
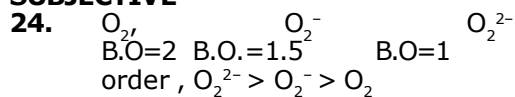
LEVEL – II

JEE ADVANCED

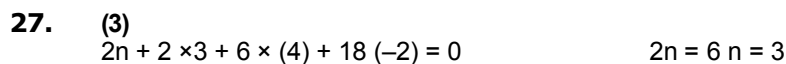
OBJECTIVE

- | | | | | | | | |
|-----------------------------------|-------------|----------|--------|-------|-------|------|------|
| 1. A | 2. A | 3. B | 4. C | 5. A | 6. B | 7. D | 8. D |
| 9. D | 10. A | 11. C | 12. D | 13. C | 14. C | | |
| 15. A-PQRT, B-QRST, C-PQR, D-PQRS | 16. A, B, C | 17. B, C | 18. D | 19. A | | | |
| 20. A-PS, B-PQRT, C-PQT, D-P | 21. B | 22. D | 23. BD | | | | |

SUBJECTIVE



Due to LP-BP repulsion the bond angle decreases, axial angle no longer remains 90° . Other angles also suffer distortion.



S-Block Elements

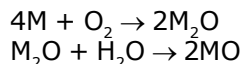
The elements in which the last electron enters the outermost s-orbital are called s-block elements. The group 1 and 2 of periodic table belong to the s-block.

Group-I Elements: (Alkali Metals)

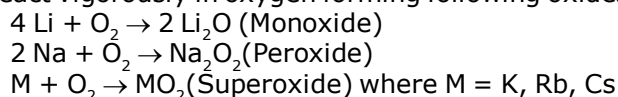
- (1) **The Elements:** are Li, Na, K, Rb, Cs Fr (Radioactive: $t_{1/2}$ of $\text{Fr}^{233} = 21$ minutes)
group-I elements are called alkali metals because they form hydroxides on reaction with water, which are alkaline in nature.
- (2) **Outer Electronic configuration:** ns^1
- (3) **Atomic and Ionic radii**
 $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$.
Increase down the group, because value of n (principal quantum number) increases.
- (4) **Density**
 $\text{Li} < \text{K} < \text{Na} < \text{Rb} < \text{Cs}$.
- (5) **Ionization Energy**
 $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$.
As size increases, I. E. decreases down the group (so Cs have lowest I. P.)
- (6) **Hardness and melting points/boiling points**
These metals are very soft and can be cut with a knife. Lithium is harder than any other alkali metal. The hardness depends upon cohesive energy
M. P. $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$
B. P. $\text{Li} > \text{Na} > \text{K} > \text{Cs} > \text{Rb}$
- (7) **Electropositive character or metallic character**
Alkali metals are strongly electropositive and metallic. Down the group electropositive nature increase so metallic nature also increases.
i.e., $\text{M} \rightarrow \text{M}^+ + \text{e}^-$
Metallic Nature : Electropositive character $\propto \frac{1}{\text{I.P.}}$
 $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$.
- (8) **Oxidation state**
Show +1 oxidation state because by losing one electron they get stable noble gas configuration.
- (9) **Photoelectric effect**
The phenomenon of emission of electrons when electromagnetic rays strikes against them is called photoelectric effect ; Alkali metal have low I. P. so show photoelectric effect.
*Cs and K are used in photoelectric cells.

Chemical Properties**(1) Reactions with air**

The alkali metals tarnish in dry air due to the formation of their oxides on their surface, which in turn react with water to form hydroxides



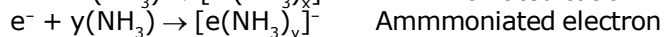
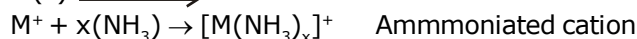
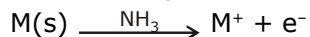
They react vigorously in oxygen forming following oxides.



- (2) **Solution in liquid NH_3**
Alkali metals dissolve in liquid ammonia (high conc. 5 M) and give blue solution which is conducting, reducing and paramagnetic in nature.

Reason

On dissolving Metal in NH_3

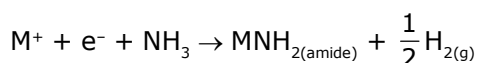


The blue colour is due to \rightarrow Ammoniated electron

The paramagnetic nature is due to \rightarrow Ammoniated electron

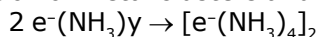
The conducting nature is due to \rightarrow Ammoniated M^+ + Ammoniated electron

- * On standing the colour fades due to formation of amide



In the absence of impurities like Fe, Pt, Zn etc, the solutions are stable.

- * In concentrated solution, the blue colour changes to bronze colour and diamagnetic due to the formation of metal clusters and ammoniated electrons also associate to form electron pairs



- (3) **Reducing Nature**

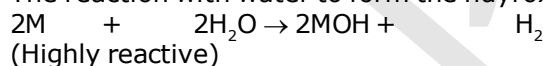
Reducing agent is electron donor.

Alkali metals are strong reducing agents with lithium being the strongest and sodium the least powerful reducing agent. $\text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{Li}$

Note : Lithium is expected to be least reducing agent due to its very high IE. However it is strongest. (due to high hydration energy).

- (4) **Reaction with H_2O**

The reaction with water to form the hydroxides having the formula MOH

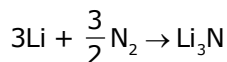


- (5) **Reaction with H_2**

They react with H_2 forming metal hydride with formula MH which are of ionic nature. Stability of hydride decreases down the group.

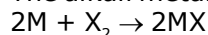
- (6) **Reaction with N_2**

Only Lithium reacts with N_2 to form ionic lithium nitride Li_3N .



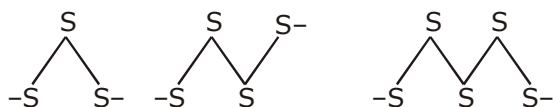
- (7) **Reaction with halogens X_2**

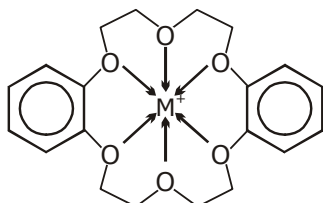
The alkali metals react vigorously with halogens to form ionic halides M^+X^-



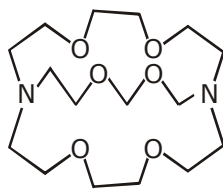
- (8) **Sulphides**

All metals react with S forming sulphides such as Na_2S and Na_2S_n ($n = 2, 3, 4, 5$ or 6). The polysulphide ions are made from zig-zag chains of sulphur atoms.



(9) **Crown Ethers and Cryptands:**

Dibenzo-18-Crown-6



Cryptand-222

$[\text{Na}(\text{Cryptand } 222)]^+\text{Na}^-$
 $[(\text{s}^+(\text{Cryptand-222}))]$

[Contains Na^- (sodide ion)]
 $[(\text{Cryptand-222})\text{e}^-]$ [electride]

Group II Elements (Alkaline earth Metals)(1) **The Elements** are Be, Mg, Ca, Sr, Ba, Ra,(2) **Outermost Electronic configuration** : - ns^2 (3) **Atomic and ionic sizes**

* The atomic and ionic radii of the alkali earth metal are smaller than corresponding alkali metals

Reason : higher nuclear charge (Z_{eff})* On moving down the group size increase, as value of n increases.
 $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ (4) **Ionization Enthalpy** $\text{Be} > \text{Mg} > \text{Ca} > \text{Sr} > \text{Ba}$

Down the group IE decreases due to increase in size

Q. IE_1 of AM $<$ IE_1 of AEM
 IE_2 of AM $>$ IE_2 of AEM
 [Where AM = Alkali metal, AEM = Alkaline earth metal]**Reason** : IE_1 to AEM is large due to increased nuclear charge in AEM as compared to AM but IE_2 of AM is large because second electron in AM is to be removed from cation which has already acquired noble gas configuration.(5) **Melting and Boiling points**

They have low m.p. and b.p. but are higher than corresponding value of group I.

Reason : They have two valency electrons which may participate in metallic bonding compared with only one electron in AM. Consequently group II elements are harder and have higher cohesive energy and \therefore have much higher m.p./b.p. than A. M.M.P. $\text{Be} > \text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$ B.P. $\text{Be} > \text{Mg} > \text{Ca} > \text{Ba} > \text{Sr}$ (6) **Electropositive and Metallic character**

Due to low IE they are strong electropositive but not as strong as AM because of comparatively high IE.

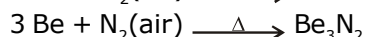
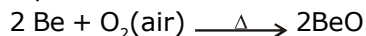
The electropositive character increase down the group.

 $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$ (7) **Oxidation state**

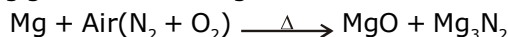
Show + 2 oxidation state.

Chemical Properties**(1) Reactivity towards Air or Oxygen**

Be and Mg are kinetically inert towards oxygen because of formation of a film of oxide on their surface. However powdered Be burn brilliantly.



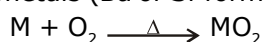
Only Mg give the following behaviour.



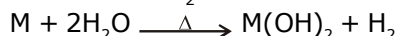
(Similar property with Li due to diagonal relation.)

* BeO, MgO are used as refractory, because these have high m.p.

* Other metals (Ba or Sr form peroxide)

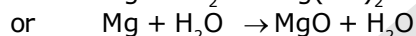
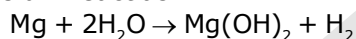
**(2) Reaction with H₂O**

AEM have lesser tendency to react with water as compared to AM. They form hydroxides and liberate H₂ on reaction with H₂O.



* Be is inert towards water.

* Magnesium react as



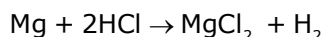
MgO forms protective layer, that is why it does not react readily unless layer is removed amalgamating with Hg.

Other metals react quite readily (Ca, Sr, Ba).

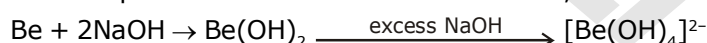
Note : Be(OH)₂ is amphoteric but other hydroxides are basic in nature.

(3) Reaction with Acids & Bases

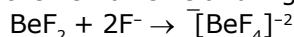
AEM react with acids & liberate H₂



Be is amphoteric as it also react with NaOH, other metals do not react as they are purely basic.

**(4) Tendency to form Complexes**

AEM have tendency to form some stable complexes. Among these Be and Mg have maximum tendency due to their small size and high charge density.



*Chlorophyll contains Mg²⁺ [Photosynthetic pigment in plants]

*Ca²⁺ and Mg²⁺ form complex with EDTA.

(5) Reactivity with NH₃

Like AM, the AEM (only Ca, Sr, Ba) dissolve in by NH₃ to give deep blue -black solutions having ammoniated cations, and ammoniated electrons.

(6) Reaction with Carbon

AEM when heated with carbon form carbides

*Be form Be₂C

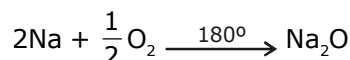
*Mg, Ca, Sr, Ba form carbides of the formula MC₂.

Group - I & II OXIDES

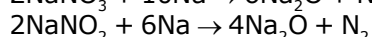
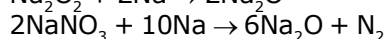
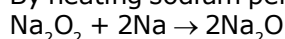
Sodium Oxide (Na₂O) :

Preparation :

- (i) It is obtained by burning sodium at 180°C in a limited supply of air or oxygen and distilling off the excess of sodium in vacuum.

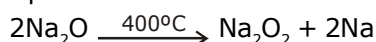


- (ii) By heating sodium peroxide, nitrate or nitrite with sodium.

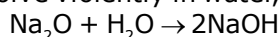


Properties :

- (i) It is white amorphous mass.
- (ii) It decomposes at 400°C into sodium peroxide and sodium

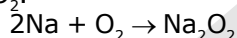


- (iii) It dissolves violently in water, yielding caustic soda.



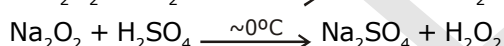
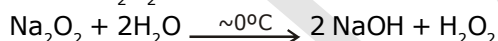
Sodium Peroxides (Na₂O₂) :

Preparation: It is formed by heating the metal in excess of air or oxygen at 300°, which is free from moisture and CO₂.

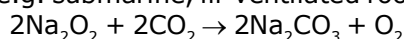


Properties :

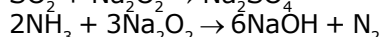
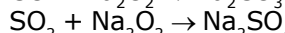
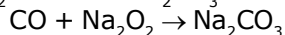
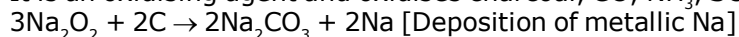
- (i) It is a pale yellow solid, becoming white in air from the formation of a film of NaOH and Na₂CO₃.
- (ii) In cold water (~ 0°C) produces H₂O but at room temperature produces O₂. In ice-cold mineral acids also produces H₂O₂.



- (iii) It reacts with CO₂, giving sodium carbonate and oxygen and hence its use for purifying air in a confined space e.g. submarine, ill-ventilated room,



- (iv) It is an oxidising agent and oxidises charcoal, CO, NH₃, SO₂



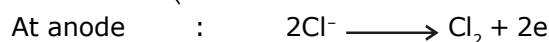
- (v) It contains peroxide ion [–O–O–]^{–2}

Uses :

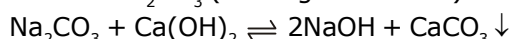
- (i) For preparing H₂O₂, O₂
- (ii) Oxygenating the air in submarines
- (iii) Oxidising agent in the laboratory.

Sodium Hydroxides :

(i) **Electrolysis of Brine:**



- (ii) Caustication of Na_2CO_3 (Gossage's method):



(suspension)

Since the $K_{sp}(\text{CaCO}_3) < K_{sp}(\text{Ca(OH)}_2)$, the reaction shifts towards right.

Properties.

- (i) It is white crystalline, deliquescent, highly corrosive solid.
- (ii) It is stable towards heat.
- (iii) It's aqueous solution alkaline in nature and soapy in touch
- (iv)
$$\text{NH}_4\text{Cl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{NH}_3 \uparrow + \text{H}_2\text{O}$$
$$\text{FeCl}_3 + 3\text{NaOH} \longrightarrow \text{Fe(OH)}_3 \downarrow + 3\text{NaCl}$$

Brown ppt

$$\text{ZnCl}_2 + 2\text{NaOH} \longrightarrow \text{Zn(OH)}_2 \downarrow + 2\text{NaCl}$$
$$\text{Zn(OH)}_2 \downarrow + 2\text{NaOH} \xrightarrow{\text{Excess}} \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O} \text{ [Same with AlCl}_3, \text{ SnCl}_2, \text{ PbCl}_2\text{]}$$

soluble
- (v) Acidic and amphoteric oxides gets dissolved easily e.g.
$$\text{CO}_2 + 2\text{NaOH} \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$
$$\text{Al}_2\text{O}_3 + 2\text{NaOH} \longrightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$$
- (vi) Aluminium and Zn metal gives H_2 from NaOH
$$2\text{Al} + 2\text{NaOH} + 2\text{H}_2\text{O} \longrightarrow 3\text{H}_2 + 2\text{NaAlO}_2$$
- (vii) Several non metals such as P, S, Cl etc. yield a hydride instead of hydrogen e.g.
$$4\text{P} + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2 \text{ (Disproportionation reaction)}$$

Potassium Hydroxide :

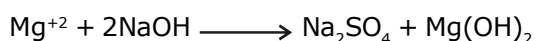
Preparation : Electrolysis of KCl aqueous solution

Properties : Same as NaOH

- *(a) It is stronger base compared to NaOH.
- (b) Solubility in water is more compared to NaOH.
- (c) In alcohol, NaOH is sparingly soluble but KOH is highly soluble.
- (d) As a reagent KOH is less frequently used but in absorption of CO_2 , KOH is preferably used compared to NaOH. Because KHCO_3 formed is soluble whereas NaHCO_3 is insoluble and may therefore choke the tubes of apparatus used.

Magnesium Hydroxide : It occurs in nature as the mineral brucite.

Preparation : It can be prepared by adding caustic soda solution to a solution of Mg-sulphate or chloride solution.



Properties:

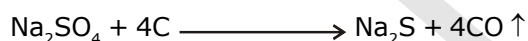
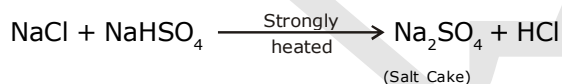
- (i) It can be dried at temperature upto 100°C only otherwise it breaks into its oxide at higher temperature. $\text{Mg(OH)}_2 \longrightarrow \text{MgO} + \text{H}_2\text{O}$
- (ii) It is slightly soluble in water imparting alkalinity.
- (iii) It dissolves in NH_4Cl solution
 $\text{Mg(OH)}_2 + 2\text{NH}_4\text{Cl} \longrightarrow \text{MgCl}_2 + 2\text{NH}_4\text{OH}$
- ** Thus, Mg(OH)_2 is not therefore precipitated from a solution of Mg^{+2} ions by NH_4OH in presence of excess of NH_4Cl .

Calcium Hydroxide :**Preparation :** By spraying water on quicklime**Properties:**

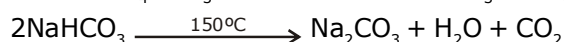
- (i) It is sparingly soluble in water.
- (ii) It's solubility in hot water is less than that of cold water. Hence solubility decreases with increase in temperature.
- (iii) It readily absorbs CO_2 as used as a test for the gas.
- (iv) it is used as a mortar.
 [Mortar is a mixture of slaked lime (1 part) and sand (3 parts) made into paste with water.]

Carbonates**Sodium Carbonate:****Preparation:**

- (i) Leblanc Process :



- (ii) Solvay Process:

**Properties :**

- (i) Anhydrous Na_2CO_3 is called as soda ash, which does not decompose on heating but melts at 852°C
- (ii) It forms number of hydrates.
 $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} \longrightarrow \text{Crystal carbonate} \longleftarrow \text{Na}_2\text{CO}_3 + \text{moisture in air}$
 $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O} \longrightarrow \text{---}$
 $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \longrightarrow \text{Washing soda}$
- (iii) Na_2CO_3 absorbs CO_2 yielding sparingly soluble sodium bicarbonate which can be calcined at 250° to get pure sodium carbonate.

$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \xrightleftharpoons{250^\circ\text{C}} 2\text{NaHCO}_3$$
- (iv) It dissolved in acid with effervescence of CO_2 and causticised by lime to give caustic soda.

$$\text{Na}_2\text{CO}_3 + \text{HCl} \longrightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$$

$$\text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \longrightarrow 2\text{NaOH} + \text{CaCO}_3$$

Uses : It is widely used in glass making as smelter .

Potassium Carbonate :

By leblance process, it can be prepared but by solvay process it cannot be prepared because KHCO_3 is soluble in water.

Properties: It resembles with Na_2CO_3 , m.p. is 900°C but a mixture of Na_2CO_3 and K_2CO_3 melts at 712°C .

Uses : It is used in glass manufacturing.

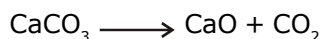
Calcium Carbonate :

It occurs in nature as marble, limestone, chalk, coral, calcite etc. It is prepared by dissolving marble or limestone in HCl and removing iron and aluminium present, by precipitating with NH_3 and then adding $(\text{NH}_4)_2\text{CO}_3$ to the solution.

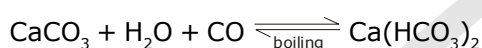


Properties:

(i) It dissociates above 1000°C as follows:



(ii) It dissolves in water containing CO_2 forming $\text{Ca}(\text{HCO}_3)_2$ but is precipitated from the solution by boiling.



Magnesium carbonate :

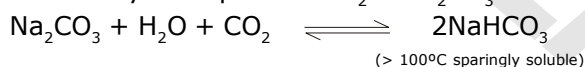
It occurs in nature as magnesite, isomorphous with calcite. It is obtained as a white precipitate by adding sodium bicarbonate to a solution of a magnesium salt; but only basic carbonate, called magnesite alba, having the approximate composition $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ is precipitated.

Properties : Same with CaCO_3

BICARBONATES

Sodium bicarbonates :

Preparation : By absorption of CO_2 in Na_2CO_3 solution.



Uses : It is used in medicine and as baking powder.

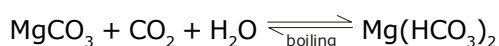
Potassium bicarbonates:

Preparation : Same NaHCO_3

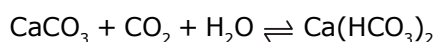
Properties : Same with NaHCO_3

But It is more alkaline and more soluble in water compared NaHCO_3 .

Magnesium bicarbonate :



Calcium bicarbonate :



Chlorides

Sodium Chloride : Prepared from brine containing 25% NaCl.

Properties:

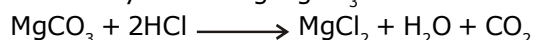
- (i) It is nonhygroscopic but the presence of MgCl_2 in common salt renders it hygroscopic.
- (ii) It is used to prepare freezing mixture in laboratory [Ice-common salt mixture is called freezing mixture and temperature goes down to -23°C .]
- (iii) For melting ice and snow on road.

Potassium Chloride : It also occurs in nature as sylvyne (KCl) or carnalite ($2\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$)

Uses : It is used as fertiliser.

Magnesium Chloride :

Preparation : By dissolving MgCO_3 in dil. HCl

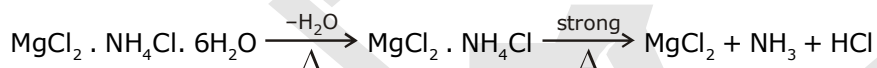


Properties :

- (i) It crystallises as hexahydrate. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- (ii) It is deliquescent solid.
- (iii) This hydrate undergoes hydrolysis as follows:

$$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \longrightarrow \text{Mg}(\text{OH})\text{Cl} + \text{HCl} + 5\text{H}_2\text{O}$$

$$\text{Mg}(\text{OH})\text{Cl} \longrightarrow \text{MgO} + \text{HCl}$$
- ** Hence, Anhydrous MgCl_2 cannot be prepared by heating this hydrate.
- ** Because of this formation of HCl. Sea water cannot be used in marine boilers which corrodes the iron body.
- (iv) Anhydrous MgCl_2 can be prepared by heating a double salt like. $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 6\text{H}_2\text{O}$ as follows:



Sorel Cement : It is a mixture of MgO and MgCl_2 (paste like) which set to hard mass on standing. This is used in dental filling, flooring etc.

Calcium chloride :

- (i) It is the by-product in solvay process.
- (ii) It may also be prepared by dissolving the carbonate in HCl .

$$\text{CaCO}_3 + 2\text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$$

Properties :

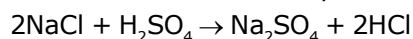
- (i) It is deliquescent crystals.
- (ii) It gets hydrolysed like MgCl_2 hence anhydrous CaCl_2 cannot be prepared.

$$\text{CaCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CaO} + 2\text{HCl}$$
 Hence, anhydrous CaCl_2 is prepared by heating $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in a current of HCl (dry)
- (iii) Anhydrous CaCl_2 is used in drying gases and organic compounds but not NH_3 or alcohol due to the formation of $\text{CaCl}_2 \cdot 8\text{NH}_3$ and $\text{CaCl}_2 \cdot 4\text{C}_2\text{H}_5\text{OH}$.

Sodium sulphate:

Preparation :

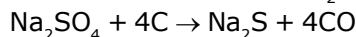
It is formed in the 1st step of leblanc process by heating common salt with sulphuric acid.



Thus the salt cake formed is crystallised out from its aqueous solution as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. This called as Glauber's salt.

- ** One interesting feature of the solubility of glauber's salt is: when crystallised at below 32.4°C , then $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is obtained but above 32.4°C , Na_2SO_4 (anh.) comes out.

Properties : It is reduced to Na_2S when fused with carbon.



Uses : It is used in medicine.

Potassium Sulphate :

It occurs in stassfurt potash beds as schonite K_2SO_4 , $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ and Kainite, $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ from which it is obtained by solution in water and crystallisation. It separates from the solution as anhydrous crystals whereas Na_2SO_4 comes as decahydrate.

Uses : It is used to prepare alum.

Magnesium Sulphate :

Preparation :

- It is obtained by dissolving kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ in boiling water and then crystallising the solution as a hepta hydrate. i.e. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. It is called as Epsom salt.
- It is also obtained by dissolving magnesite in hot dil. H_2SO_4 .

$$\text{MgCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{H}_2\text{O} + \text{CO}_2$$
- Or by dissolving dolomite (CaCO_3 , MgCO_3) in hot dil. H_2SO_4 and removing the insoluble CaSO_4 by filtration.
- It is isomorphous with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

Calcium Sulphate : It occurs as anhydrite CaSO_4 and as the dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, gypsum, alabaster or satin-spar.

Properties :

- Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) $\xrightleftharpoons[+\text{H}_2\text{O}]{120^{\circ}\text{C}}$ $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ (Plaster of paris)
 $\downarrow 200^{\circ}\text{C}$
 (anhydrous) CaSO_4
 Dead burnt. plaster
- Solubility of CaSO_4 at first increases upto a certain point and then decreases with rise of temperature.
- Plaster paris is used in mould making due to its porous body.

EXERCISE – I

OBJECTIVE PROBLEMS (JEE MAIN)

1. Cs^+ ions impart violet to Bunsen flame. This is due to the fact that the emitted radiations are of
 (A) high energy
 (B) lower frequencies
 (C) longer wave-lengths
 (D) zero wave number

Sol.

2. The compound (s) of alkaline earth metals, which are amphoteric in nature is/are-
 (A) BeO (B) MgO
 (C) $\text{Be}(\text{OH})_2$ (D) $\text{Mg}(\text{OH})_2$

Sol.

3. An alkaline earth metal (M) gives a salt with chlorine, which is soluble in water at room temperature. It also forms an insoluble sulphate whose mixture with a sulphide of a transition metal is called 'lithopone'—a white pigment. Metal M is-
 (A) Ca (B) Mg
 (C) Ba (D) Sr

Sol.

4. The reaction of an element A with water produces combustible gas B and an aqueous solution of C. When another substance D reacts with this solution C also produces the same gas B. D also produces the same gas even on reaction with dilute H_2SO_4 at room temperature. Element A imparts golden yellow colour to Bunsen flame. Then A, B, C and D may be identified as
 (A) Na, H_2 , NaOH and Zn
 (B) K, H_2 , KOH and Zn
 (C) K, H_2 , NaOH and Zn
 (D) Ca, H_2 , CaCO_3 and Zn

Sol.

5. The hydroxide of alkaline earth metal, which has the lowest value of solubility product (K_{sp}) at normal temperature (25°C) is-
 (A) $\text{Ca}(\text{OH})_2$ (B) $\text{Mg}(\text{OH})_2$
 (C) $\text{Sr}(\text{OH})_2$ (D) $\text{Be}(\text{OH})_2$

Sol.

6. (Yellow ppt) T $\xleftarrow{\text{K}_2\text{CrO}_4/\text{H}^+}$ X $\xrightarrow{\text{dil. HCl}}$ Y.
 (Yellow ppt) + Z↑ (pungent smelling gas)
 If X gives green flame test. Then, X is :
 (A) MgSO_4 (B) BaSO_4
 (C) CuSO_4 (D) PbSO_4

Sol.

7. Which of the following carbonate of alkali metals has the least thermal stability ?
 (A) Li_2CO_3 (B) K_2CO_3
 (C) Cs_2CO_3 (D) Na_2CO_3

Sol.

8. The 'milk of magnesia' used as an antacid is chemically -
 (A) $\text{Mg}(\text{OH})_2$ (B) BaSO_4
 (C) MgCl_2 (D) $\text{MgO} + \text{MgCl}_2$

Sol.

9. The alkali metals which form normal oxide, peroxide as well as super oxides are-
 (A) Na, Li (B) K, Li
 (C) Li, Cs (D) K, Rb

Sol.

10. The pair of compounds, which cannot exist together in a solution is-
- (A) NaHCO_3 and NaOH
 (B) Na_2CO_3 and NaOH
 (C) NaHCO_3 and Na_2CO_3
 (D) NaHCO_3 and H_2O

Sol.

11. $\text{Mg}_2\text{C}_3 + \text{H}_2\text{O} \rightarrow \text{X}$ (organic compound). Compound X is-

- (A) C_2H_2 (B) CH_4
 (C) propyne (D) ethene

Sol.

12. The hydration energy of Mg^{2+} is-

- (A) more than that of Mg^{3+} ion
 (B) more than that of Na^+ ion
 (C) more than that of Al^{3+} ion
 (D) more than that of Be^{3+} ion

Sol.

13. The golden yellow colour associated with NaCl to Bunsen flame can be explained on the basis of-

- (A) low ionisation potential of sodium
 (B) emission spectrum
 (C) photosensitivity of sodium
 (D) sublimation of metallic sodium of yellow vapours

Sol.

14. Solution of sodium metal in liquid ammonia is a strong reducing agent due to presence of-

- (A) solvated sodium ions
 (B) solvated hydrogen ions
 (C) sodium atoms or sodium hydroxide
 (D) solvated electrons

Sol.

15. The order of solubility of lithium halides in non-polar solvents follows the order :

- (A) $\text{LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$
 (B) $\text{LiF} > \text{LiI} > \text{LiBr} > \text{LiCl}$
 (C) $\text{LiCl} > \text{LiF} > \text{LiI} > \text{LiBr}$
 (D) $\text{LiBr} > \text{LiCl} > \text{LiF} > \text{LiI}$

Sol.

16. The salt which finds uses in qualitative inorganic analysis is-

- (A) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$
 (B) $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
 (C) $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$
 (D) $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$

Sol.

17. Fire extinguishers contain -

- (A) conc. H_2SO_4 solution
 (B) H_2SO_4 and NaHCO_3 solutions
 (C) NaHCO_3 solution
 (D) CaCO_3 solution

Sol.

18. CsBr_3 contains -

- (A) Cs-Br covalent bonds
 (B) Cs^{3+} and Br^- ions
 (C) Cs^+ and Br_3^- ions
 (D) Cs^{3+} and Br_3^{3-} ions

Sol.

19. $\text{Na} + \text{Al}_2\text{O}_3 \xrightarrow{\text{High temperature}} \text{X} \xrightarrow[\text{water}]{\text{CO}_2 \text{ in}} \text{Y}$; compound Y is-

- (A) NaAlO_2 (B) NaHCO_3
 (C) N_2CO_3 (D) Na_2O_2

Sol.

20. The correct order of second ionisation potentials (IP) of Ca, Ba and K is-

- (A) $\text{K} > \text{Ca} > \text{Ba}$ (B) $\text{Ba} > \text{Ca} > \text{K}$
 (C) $\text{K} > \text{Ba} > \text{Ca}$ (D) $\text{K} = \text{Ba} = \text{Ca}$

Sol.

21. EDTA is used in the estimation of-

- (A) Mg^{2+} ions
 (B) Ca^{2+} ions
 (C) both Ca^{2+} and Mg^{2+} ions
 (D) Mg^{2+} ions but not Ca^{2+} ions

Sol.

22. $\text{aq. NaOH} + \text{P}_4 \text{ (white)} \rightarrow \text{PH}_3 + \text{X}$; compound X is

- (A) NaH_2PO_2 (B) NaHPO_4
 (C) Na_2CO_3 (D) NaHCO_3

Sol.

23. The correct order of solubility is-

- (A) $\text{CaCO}_3 < \text{KHCO}_3 < \text{NaHCO}_3$
 (B) $\text{KHCO}_3 < \text{CaCO}_3 < \text{NaHCO}_3$
 (C) $\text{NaHCO}_3 < \text{CaCO}_3 < \text{KHCO}_3$
 (D) $\text{CaCO}_3 < \text{NaHCO}_3 < \text{KHCO}_3$

Sol.

24. The complex formation tendency of alkaline earth metals decreases down the group because-

- (A) atomic size increases
 (B) availability of empty d and f-orbitals increases
 (C) nuclear charge to volume ratio increases
 (D) all the above

Sol.

25. The alkaline earth metals, which do not impart any colour to Bunsen flame are-

- (A) Be and Mg (B) Mg and Ca
 (C) Be and Ca (D) Be and Ba

Sol.

26. $\text{Y} \xleftarrow{\Delta, 205^\circ\text{C}} \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \xleftarrow{\Delta, 120^\circ\text{C}} \text{X}$. X and Y are respectively-

- (A) plaster of paris, dead burnt plaster
 (B) dead burnt plaster, plaster of paris
 (C) CaO and plaster of paris
 (D) plaster of paris, mixture of gases

Sol.

27. A metal M readily forms water soluble sulphate, and water insoluble hydroxide $\text{M}(\text{OH})_2$. Its oxide MO is amphoteric, hard and having high melting point. The alkaline earth metal M must be-

- (A) Mg (B) Be
 (C) Ca (D) Sr

Sol.

28. When K_2O is added to water, the solution becomes basic in nature because it contains a significant concentration of-

- (A) K^+ (B) O^{2-}
 (C) OH^- (D) O_2^{2-}

Sol.

29. $(\text{White ppt}) \text{D} \xleftarrow{\text{Na}_2\text{CO}_3} \text{A} \xrightarrow[\text{(in acetic acid)}]{\text{K}_2\text{CrO}_4} \text{B} (\text{Yellow ppt})$
 $\text{dil. H}_2\text{SO}_4 \downarrow$
 C (White ppt)

If A is the metallic salt, then the white ppt. of D must be of-

- (A) strontium carbonate
 (B) red lead
 (C) barium carbonate
 (D) calcium carbonate

Sol.

30. (Mily Cloud) $\text{C} \xleftarrow{\text{CO}_2} \text{A} + \text{Na}_2\text{CO}_3 \rightarrow \text{B} + \text{C}$

The chemical formulae of A and B are-

- (A) NaOH and $\text{Ca}(\text{OH})_2$
 (B) $\text{Ca}(\text{OH})_2$ and NaOH
 (C) NaOH and CaO
 (D) CaO and $\text{Ca}(\text{OH})_2$

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. An aqueous solution of an halogen salt of potassium reacts with same halogen X_2 to give KX_3 , a brown coloured solution, in which halogen exists as X_3^- ion, X_2 as a Lewis acid and X^- as a Lewis base, halogen X is-

(A) chlorine (B) bromine
(C) iodine (D) fluorine

Sol.

2. The correct order of basic-strength of oxides of alkaline earth metals is-

(A) $BeO > MgO > CaO > SrO$
(B) $SrO > CaO > MgO > BeO$
(C) $BeO > CaO > MgO > SrO$
(D) $SrO > MgO > CaO > BeO$

Sol.

3. The order of melting point of chlorides of alkali metals is-

(A) $LiCl > NaCl > KCl < CaCl$
(B) $LiCl > NaCl > KCl > CsCl$
(C) $NaCl > KCl > CsCl > LiCl$
(D) $LiCl > NaCl > CsCl > KCl$

Sol.

4. $NaOH(\text{Solid}) + CO \xrightarrow{200^\circ C} X$; product X is-

(A) $NaHCO_3$ (B) Na_2CO_3
(C) $HCOONa$ (D) H_2CO_3

Sol.

5. $X \xrightarrow{N_2, \Delta} Y \xrightarrow{H_2O} Z$ (colourless gas) $\xrightarrow{CuSO_4}$ T (blue colour)

Then, substances Y and T are-

(A) $Y = Mg_3N_2$ and $T = CuSO_4 \cdot 5H_2O$
(B) $Y = Mg_3N_2$ and $T = CuSO_4 \cdot 4NH_3$
(C) $Y = Mg(NO_3)_2$ and $T = CuO$
(D) $Y = MgO$ and $T = CuSO_4 \cdot 4NH_3$

Sol.

6. Weakest base among KOH , $NaOH$, $Ca(OH)_2$ and $Zn(OH)_2$ is-

(A) $Ca(OH)_2$ (B) KOH
(C) $NaOH$ (D) $Zn(OH)_2$

Sol.

7. If X and Y are the second ionisation potentials of alkali and alkaline earth metals of same period, then-

(A) $X > Y$ (B) $X < Y$
(C) $X = Y$ (D) $X \ll Y$

Sol.

8. The aqueous solutions of lithium salts are poor conductor of electricity rather than other alkali metals because of-

(A) high ionisation energy
(B) high electronegativity
(C) lower ability of Li^+ ions to polarize water molecules
(D) higher degree of hydration of Li^+ ions

Sol.

9. Sodium metal is highly reactive and cannot be stored under-

(A) toluene (B) kerosene oil
(C) alcohol (D) benzene

Sol.

10. Nitrogen dioxide cannot be prepared by heating -

- (A) KNO_3 (B) AgNO_3
(C) $\text{Pb}(\text{NO}_3)_2$ (D) $\text{Cu}(\text{NO}_3)_2$

Sol.

11. In LiAlH_4 , metal Al is present in-

- (A) anionic part
(B) cationic part
(C) in both anionic and cationic part
(D) neither in cationic nor in anionic part

Sol.

12. $\text{X} \xrightarrow{\text{CoCl}_2} \text{CaCl}_2 + \text{Y} \uparrow$; the effective ingredient of X is-

- (A) OCl^- (B) Cl^-
(C) OCl^+ (D) OCl_2^-

Sol.

13. Which one of the following fluoride of alkali metals has the highest lattice energy?

- (A) LiF (B) CsF
(C) NaF (D) KF

Sol.

14. Crown ethers and cryptands form -

- (A) Complexes with alkali metals
(B) salts of alkali metals
(C) hydroxides of alkali metals used for inorganic quantitative analysis
(D) organic salts of alkali metals

Sol.

15. White heavy precipitates are formed when BaCl_2 is added to a clear solution of compound A. Precipitates are insoluble in dilute HCl . Then, the compound A is-

- (A) a bicarbonate (B) a carbonate
(C) a sulphate (D) a chloride

Sol.

16. Among MgCl_2 , RbCl , BeCl_2 and LiCl , the compounds with the highest and the lowest % of ionic characters are-

- (A) MgCl_2 and BeCl_2 (B) RbCl_2
(C) BeH_2 (D) AlCl_3

Sol.

17. $\text{X} + \text{C} + \text{Cl}_2 \xrightarrow[\text{of about } 1000\text{K}]{\text{High temperature}} \text{Y} : \text{CO}; \text{Y} + 2\text{H}_2\text{O} \rightarrow \text{Z} + 2\text{HCl}$

Compound Y is found in polymeric chain structure and is an electron deficient molecule. Y must be-

- (A) BeO (B) BeCl_2
(C) BeH_2 (D) AlCl_3

Sol.

18. The correct order of degree of hydration of M^+ ions of alkali metals is-

- (A) $\text{Li}^+ < \text{K}^+ < \text{Na}^+ < \text{Rb}^+ < \text{Cs}^+$
(B) $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$
(C) $\text{Cs}^+ < \text{Rb}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+$
(D) $\text{Cs}^+ < \text{Rb}^+ < \text{Na}^+ < \text{K}^+$

Sol.

19. $\text{BeCl}_2 + \text{LiAlH}_4 \rightarrow \text{X} + \text{LiCl} + \text{AlCl}_3$

- (A) X is LiH (B) X is BeH_2
(C) X is $\text{BeCl}_2 \cdot 2\text{H}_2\text{O}$ (D) None

Sol.

20. The order of thermal stability of carbonates of IIA group is-

- (A) $\text{BaCO}_3 > \text{SrCO}_3 > \text{CaCO}_3 > \text{MgCO}_3$
 (B) $\text{MgCO}_3 > \text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3$
 (C) $\text{CaCO}_3 > \text{SrCO}_3 > \text{BaCO}_3 > \text{MgCO}_3$
 (D) $\text{MgCO}_3 = \text{CaCO}_3 > \text{SrCO}_3 = \text{BaCO}_3$

Sol.

21. A pair of substances which gives the same products on reaction with water is-

- (A) Mg and MgO (B) Sr and SrO
 (C) Ca and CaH_2 (D) Be and BeO

Sol.

22. Which of the following is not a anomalous property of lithium ?

- (A) Hydrated lithium ion is the largest among alkali metals
 (B) The melting and boiling points of lithium are comparatively high
 (C) Lithium is softer than that of other alkali metals
 (D) The ionisation potential and electronegativity of lithium are higher than those of other alkali metals

Sol.

23. The incorrect statement (s) is/are-

- (A) Mg cannot form complexes
 (B) Be can form complexes due to a very small atomic size
 (C) the first ionisation potential of Be is higher than that of Mg
 (D) Mg forms an alkaline hydroxide while Be forms amphoteric oxides

Sol.

24. The commercial method of preparation of potassium by reduction of molten KCl with metallic sodium at 850°C is based on the fact that-

- (A) potassium is solid and sodium distills off at 850°C
 (B) potassium being more volatile and distills off thus shifting the reaction forward
 (C) sodium is more reactive than potassium at 850°C
 (D) sodium has less affinity to chloride ions in the presence of potassium ion

Sol.

25. $\text{Be}_2\text{C} + \text{H}_2\text{O} \rightarrow \text{BeO} + \text{X}$

$\text{CaC}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{Y}$; then X and Y respectively-

- (A) CH_4 , CH_4 (B) CH_4 , C_2H_6
 (C) CH_4 , C_2H_2 (D) C_2H_2 , CH_4

Sol.

26. Which of the following groups of elements have chemical properties that are most similar-

- (A) Na, K, Ca (B) Mg, Sr, Ba
 (C) Be, Al, Ca (D) Be, Ra, Cs

Sol.

27. MgBr_2 and MgI_2 are soluble in acetone because of

- (A) Their ionic nature
 (B) Their coordinate nature
 (C) Their metallic nature
 (D) Their covalent nature

Sol.

28. Which of the following is not the characteristic of barium ?

- (A) It emits electrons on exposure to light
 (B) It is a silvery white metal
 (C) It forms $\text{Ba}(\text{NO}_3)_2$ which is used in preparation of green fire
 (D) Its ionization potential is lower than radium.

Sol.

EXERCISE – III

OBJECTIVE PROBLEMS (JEE ADVANCED)

Question No. 1 to 7

Questions given below consist of two statements each printed as Assertion (A) and Reason (R) ; while answering these questions you are required to choose any one of the following four responses :

- (A) If both (A) and (R) are true and (R) is the correct explanation of (A)
 (B) If both (A) and (R) are true but (R) is not correct explanation of (A)
 (C) If (A) is true but (R) is false
 (D) If (A) is false and (R) is true

1. **Assertion :** Beryllium does not impart any characteristic colour to the bunsen flame.

Reason : Due to its very high ionization energy, beryllium requires a large amount of energy for excitation of the electrons.

Sol.

2. **Assertion :** In fused state, calcium chloride cannot be used to dry alcohol or NH_3 .

Reason : Anhyd. CaCl_2 is not good desiccant.

Sol.

3. **Assertion :** Diagonal relationship is shown between Be and Al.

Reason : Ionization potential of Be is almost the same as that of Al.

Sol.

4. **Assertion :** Beryllium halides dissolve in organic solvents.

Reason : Beryllium halides are ionic in character.

Sol.

5. **Assertion :** BeCl_2 fumes in moist air.

Reason : BeCl_2 reacts with moisture to form HCl gas.

Sol.

6. **Assertion :** Calcium carbide on hydrolysis gives methane.

Reason : Calcium carbide contains C_2^{2-} anion.

Sol.

7. **Assertion :** When CO_2 is passed through lime water, it first turns milky and then the solution becomes clear when the passage of CO_2 is continued.

Reason : the milkiness is due to the formation of insoluble CaCO_3 which then changes to soluble $\text{Ca}(\text{HCO}_3)_2$ when excess of CO_2 is present.

Sol.

8. **Assertion :** MgCO_3 is soluble in water when a current of CO_2 is passed.

Reason : The solubility of MgCO_3 is due to the formation of $\text{Mg}(\text{HCO}_3)_2$.

Sol.

9. The correct statement is/are-

- (A) BeCl_2 is a covalent compound
 (B) BeCl_2 is an electron deficient molecule
 (C) BeCl_2 can form dimer
 (D) the hybrid state of Be in BeCl_2 is sp^2

Sol.

10. KO_2 finds use in oxygen cylinders used for space and submarines. The fact(s) related to such use of KO_2 is/are-

- (A) it produces O_2
 (B) it produces O_3
 (C) it absorbs CO_2
 (D) it absorbs both CO and CO_2

Sol.

11. The compound(s) which have $-\text{O}-\text{O}-$ bond(s) is/are-

- (A) BaO_2 (B) Na_2O_2
 (C) CrO_5 (D) Fe_2O_3

Sol.

12. Highly pure dilute solution of sodium in ammonia -
 (A) shows blue colouration due to solvated electrons
 (B) shows electrical conductivity due to both solvated electrons as well as solvated sodium ions
 (C) shows red colouration due to solvated electrons but a bad conductor of electricity
 (D) produces hydrogen gas or carbonate

Sol.

13. Which of the following compounds are paramagnetic in nature ?
 (A) KO_2 (B) K_2O_2
 (C) Na_2O_2 (D) RbO_2

Sol.

14. Which of the following substance(s) is/are used in laboratory for drying purposes ?
 (A) anhydrous P_2O_5 (B) graphite
 (C) anhydrous CaCl_2 (D) Na_3PO_4

Sol.

15. Na_2SO_4 is water soluble but BaSO_4 is insoluble because-
 (A) the hydration energy of Na_2SO_4 is higher than that of its lattice energy
 (B) the hydration energy of Na_2SO_4 is less than that of its lattice energy

- (C) the hydration energy of BaSO_4 is less than that of its lattice energy
 (D) the hydration energy of BaSO_4 is higher than that of its lattice energy

Sol.

16. Which of the following statement are false ?
 (A) BeCl_2 is a linear molecule in the vapour state but it is polymeric in the solid state
 (B) Calcium hydride is called hydrolith
 (C) Carbides of both Be and Ca react with water to form acetylene
 (D) Oxides of both Be and Ca are amphoteric.

Sol.

17. Which of the following are ionic carbides ?
 (A) CaC_2 (B) Al_4C_3
 (C) SiC (D) Be_2C

Sol.

18. The compound(s) formed upon combustion of sodium metal in excess air is (are)-
 (A) Na_2O_2 (B) Na_2O
 (C) NaO_2 (D) NaOH

Sol.

s-Block Elements

18. Which one of the following statements is true for all the alkali metals?
 (A) Their nitrates decompose on heating to give NO_2 and O_2 .
 (B) Their carbonates decompose on heating to give CO_2 and normal oxide.
 (C) They react with halogens to give the halides of the type, MX .
 (D) They react with oxygen to give mainly the oxide, M_2O .

Sol.

19. The electrolyte used in Castner's process of sodium extraction is :
 (A) Anhydrous Na_2CO_3
 (B) Aqueous NaOH
 (C) $\text{NaCl} + \text{CaCl}_2$
 (D) Fused Anhydrous NaOH

Sol.

20. Based on lattice energy and other considerations which one of the following alkali metal chloride is expected to have highest melting point?
 (A) LiCl (B) NaCl
 (C) KCl (D) RbCl

Sol.

21. Select correct statement :
 (A) Oxides (M_2O) and peroxides (M_2O_2) of alkali metals are diamagnetic and colourless.
 (B) Superoxides (MO_2) of alkali metals are paramagnetic.

- (C) Li and Na do not form superoxides.
 (D) All are correct.

Sol.

22. Which of the following salt does not form any precipitate with excess of NaOH ?
 (A) ZnCl_2 (B) FeCl_3
 (C) CrCl_3 (D) CuSO_4

Sol.

23. The correct order of stability of hydrides of alkali metals is :
 (A) $\text{LiH} > \text{NaH} > \text{KH} > \text{RbH}$
 (B) $\text{NaH} > \text{KH} > \text{RbH} > \text{LiH}$
 (C) $\text{RbH} > \text{KH} > \text{NaH} > \text{LiH}$
 (D) $\text{LiH} > \text{RbH} > \text{KH} > \text{NaH}$

Sol.

24. The correct order of mobility of alkali metal ions in aqueous solution is :
 (A) $\text{K}^+ > \text{Rb}^+ > \text{Na}^+ > \text{Li}^+$
 (B) $\text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
 (C) $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$
 (D) $\text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Li}^+$

Sol.

25. Pick out statement(s) which is (are) not true about diagonal relationship of Li and Mg :
- A.** Polarising powers of Li^+ and Mg^{2+} ions are almost same
B. Like Li, Mg decomposes water very fast
C. LiCl and MgCl_2 are deliquescent
D. Like Li, Mg readily reacts with liquid bromine at ordinary temperature
- (A) A and D (B) B and C
 (C) Only B (D) B and D

Sol.

Sol.

29. Several blocks of magnesium are fixed to the bottom of a ship to :
- (A) prevent action of water and salt
 (B) prevent puncturing by under sea rocks
 (C) keep away the sharks
 (D) make the ship lighter

Sol.

26. Which of the following carbides give allylene on hydrolysis ?
- (A) CaC_2 (B) Be_2C
 (C) MgC_2 (D) Mg_2C_3

Sol.

27. Black ash is :
- (A) $\text{CaS} + \text{NaHCO}_3$ (B) $\text{CaSO}_4 + \text{NaCO}_3$
 (C) $\text{CaSO}_4 + \text{NaHCO}_3$ (D) $\text{CaS} + \text{Na}_2\text{CO}_3$

Sol.

30. A solid compound 'X' on heating gives CO_2 gas and a residue. The residue mixed with water forms 'Y'. On passing an excess of CO_2 through 'Y' in water a clear solution 'Z' is obtained. On boiling 'Z' compound 'X' is reformed. The compound 'X' is :
- (A) $\text{Ca}(\text{HCO}_3)_2$ (B) CaCO_3
 (C) Na_2CO_3 (D) CaSO_4

Sol.

28. Magnesium is an important component of which biomolecule occurring extensively in living world ?
- (A) Haemoglobin (B) ATP
 (C) Chlorophyll (D) Vitamin B_{12}

EXERCISE – IV

PREVIOUS YEARS

LEVEL – I

JEE MAIN

Q.1 A metal M readily forms its sulphate MSO_4 which is water soluble. It forms oxide MO which becomes inert on heating. It forms insoluble hydroxide which is soluble in NaOH. The metal M is -

[AIEEE-02]

- (A) Mg
(C) Ca

- (B) Ba
(D) Be

Sol.

Q.2 KO_2 is used in space and submarines because it -

[AIEEE-02]

- (A) Absorbs CO_2 and increase O_2 concentration
(B) Absorbs moisture
(C) Absorbs CO_2
(D) Produces ozone

Sol.

Q.3 In current cement plasters, water is sprinkled from time to time. This helps in - [AIEEE-03]

- (A) Hydrating sand and gravel mixed with cement
(B) Converting sand into silicate
(C) Developing interlocking needle like crystals of hydrated silicates
(D) Keeping it cool

Sol.

Q.4 The solubilities of carbonates decreases down the magnesium group due to decrease in -

[AIEEE-03]

- (A) Inter-ionic attraction
(B) Entropy of solution formation
(C) Lattice energy of solids
(D) Hydration energy of cations

Sol.

Q.5 The substance not likely to contain $CaCO_3$ is - [AIEEE-03]

- (A) Sea shells
(B) Dolomite
(C) A marble statue
(D) Calcined gypsum

Sol.

Q.6 One mole of magnesium nitride on reaction with excess of water gives - [AIEEE-04]

- (A) Two mole of HNO_3
(B) Two mole of NH_3
(C) 1 mole of NH_3
(D) 1 mole of HNO_3

Sol.

Q.7 Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in **[AIEEE- 04]**

- (A) Show maximum covalency in compounds
- (B) Chlorides of both form dimer
- (C) Forming covalent halides
- (D) Show amphoteric nature in their oxides

Sol.

Q.8 A piece of magnesium ribbon was heated to redness in an atmosphere of nitrogen and on cooling water was added, the gas evolved was **[AIEEE -05]**

- (A) Ammonia
- (B) Hydrogen
- (C) Nitrogen
- (D) Oxygen

Sol.

Q.9 The ionic mobility of alkali metal ions in aqueous solution is maximum for - **[AIEEE -06]**

- (A) Rb^+
- (B) Li^+
- (C) Na^+
- (D) K^+

Sol.

Q.10 The products obtained on heating LiNO_3 will be- **[AIEEE -2011]**

- (A) $\text{Li}_2\text{O} + \text{NO}_2 + \text{O}_2$
- (B) $\text{Li}_3\text{N} + \text{O}_2$
- (C) $\text{Li}_2\text{O} + \text{NO} + \text{O}_2$
- (D) $\text{LiNO}_2 + \text{O}_2$

Sol.

Q.11 What is the best description of the change that occurs when $\text{Na}_2\text{O}(\text{s})$ is dissolved in water ? **[AIEEE -2011]**

- (A) Oxide ion accepts sharing in a pair of electrons
- (B) Oxide ion donates a pair of electrons
- (C) Oxidation number of oxygen increases
- (D) Oxidation number of sodium decreases

Sol.

Q.12 Which of the following on thermal-decomposition yields a basic as well as an acidic oxide ? **[AIEEE-2012]**

- (A) KClO_3
- (B) CaCO_3
- (C) NH_4NO_3
- (D) NaNO_3

Sol.

LEVEL – II

JEE ADVANCED

Q.1 Highly pure dilute solution of sodium in liquid ammonia - **[IIT-08]**

- (A) Show blue colour
- (B) exhibits electrical conductivity
- (C) Produce sodium amide
- (D) Produce hydrogen gas

Sol.

Q.2 **STATEMENT -1** : Alkali metals dissolve in liquid ammonia to give blue solutions.

[IIT - 2007]

STATEMENT -2 : Alkali metals in liquid ammonia give solvated species of the type $[M(NH_3)_n]^+$ (M = alkali metals).

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
- (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
- (C) Statement-1 is True, Statement-2 is False
- (D) Statement-1 is False, Statement-2 is True

Sol.

Q.3 The compounds(s) formed upon combustion of sodium metal in excess of air is(are)-

[IIT - 2009]

- (A) Na_2O_2
- (B) Na_2O
- (C) NaO_2
- (D) $NaOH$

Sol.

Answers

Exercise-I

1. A	2. AC	3. C	4. A	5. D
6. B	7. A	8. A	9. D	10. A
11. C	12. B	13. A	14. D	15. A
16. C	17. B	18. C	19. C	20. A
21. C	22. A	23. D	24. A	25. A
26. A	27. B	28. C	29. C	30. B

Exercise-II

1. C	2. D	3. C	4. A	5. D
6. D	7. D	8. D	9. C	10. A
11. A	12. A	13. A	14. A	15. C
16. B	17. B	18. C	19. B	20. B
21. C	22. A	23. B	24. C	25. C
26. D	27. AD	28. A		

Exercise-III

1. A	2. B	3. C	4. C	5. A
6. D	7. A	8. A	9. ABC	10. AC
11. ABC	12. AD	13. A	14. AC	15. CD
16. CD	17. ABD	18. AC	19. D	20. A
21. ABD	22. AC	23. AC	24. B	25. D
26. D	27. D	28. C	29. A	30. B

Exercise-IV

Level-I

Q.No.	1	2	3	4	5	6	7	8	9	10	11	12
Ans.	D	A	C	D	D	B	A	A	A	A	B	B

Level-II

Q.No.	1	2	3
Ans.	A,B	B	A,B

GASEOUS STATE

1. Introduction

A given substance may occur in solid, liquid or gaseous phase depending upon the relative value of two tendencies namely Mutual Attraction (MA) and Escaping Tendency (ET)

- (i) if MA is greater than ET then substance will occur in solid state
 - (ii) if MA is slightly greater than ET then substance will occur in liquid state
 - (iii) if MA is very much less than ET then substance will occur in gaseous state
- Out of the three states of matter, the most simplest one is the gaseous state.

The state is characterized by sensitivity of volume change with change of pressure and temperature. It is due to large distance between molecules as compared to their own dimensions. There exist weak Vander Waal's forces, molecules move independent of each other with speed about 400 ms^{-1} . Gases show maximum equality in their behavior irrespective of their nature.

2. Measurable properties of gases

1. Mass

Def. The gases do possess mass. The mass of gas is generally used in the form of number of moles which is related as

$$(i) \quad \text{no. of moles} = \frac{\text{wt. in gm}}{\text{molecular mass of gases}} \left(n = \frac{w}{M} \right)$$

Two other useful formulae to calculate number of moles of gas are –

$$(ii) \quad \text{number of moles} = \frac{\text{no. of molecules of given gas}}{\text{Avogadro's number of molecules}} \left(n = \frac{N}{N_A} \right)$$

$$(iii) \quad \text{no. of moles} = \frac{\text{volume of given gas in litres at STP}}{22.4 \text{ L}}$$

When container contains more than one gas then molecular mass of mixture is termed as effective molecular mass (EMM) which is intermediate between molecular masses of all the gases present in the container.

$$\text{Effective molecular mass} = \frac{\text{Total mass of all the gases present in the container}}{\text{Total no. of moles of all gases present in the container}}$$

2. Volume

Def. Volume of gas is nothing but volume of the container in which it is present.

Relation between different units of volume

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^3 \text{ litre} = 10^6 \text{ cm}^3 = 10^6 \text{ ml} = 10^9 \text{ mm}^3.$$

3. Temperature

Def. Degree of hotness or coldness of a body is measured by temperature

$$\frac{C}{100} = \frac{K - 273}{100} = \frac{F - 32}{180}$$

C – Celcius scale, K – Kelvin scale, F – Fahrenheit scale

Note : In all the problems of gaseous state (i.e. in all gas law equations), temperature must be expressed in kelvin scale. i.e. , $t^\circ\text{C} + 273 = \text{TK}$

4. Pressure**Def.** Force acting per unit area

$$P = \frac{F}{A}$$

Units :

CGS : dyne/cm²
 MKS : Newton/m² (1N/m² = 1Pa)
 Relation : 1 N/m² = 10 dyne/cm²

Units of pressure :

1 atm = 76 cm of Hg
 = 760 mm of Hg
 = 760 torr
 = 1.01325 × 10⁵ N/m²
 = 101.325 kPa
 = 1.01325 bar
 = 14.7 lb/in² (Psi)
 = 10.33 meters of H₂O

5. Density**Def.** Mass per unit volume

$$d = \frac{m}{V}$$

Units :

CGS : g/cm³
 MKS : kg/m³
 Relation : 1 kg/m³ = 10⁻³ g/cm³

Density of gases**Absolute density**

(mass per unit volume)

(i) $d = \frac{m}{V}$

(ii) unit : g/l

(iii) function of temp., pressure, no. of moles

Relative density

(Relative to hydrogen turned as vapour density)

(i) $VD = \frac{\text{molecular mass}}{2}$

(ii) No unit

(iii) independent of Pressure, Temperature

Note : Mass, volume and no. of moles are extensive properties that depend on mass hence then all divertly additive in nature.

Note : Density, Pressure and Temperature are intensive properties they does not depend on mass hence they are non-additive in nature.

3. The Gas Laws**(i) Boyle's Law :**

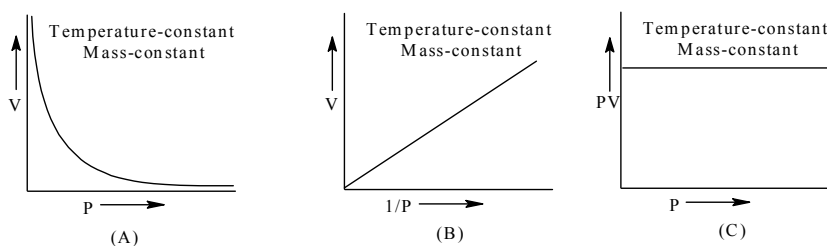
It relates the volume and the pressure of a given mass of a gas at constant temperature. Boyle's law states that, "at constant temperature, the volume of a sample of a gas varies inversely with the pressure".

$\therefore P \propto \frac{1}{V}$ (when temperature and number of moles are kept constant)

The proportionality can be changed into an equality by introducing a constant k, i.e.,

$$P = \frac{k}{V} \text{ or } PV = k$$

Boyle's law can be verified by any one of the following three ways graphically.



Alternatively, Boyle's law can also be stated as follows :

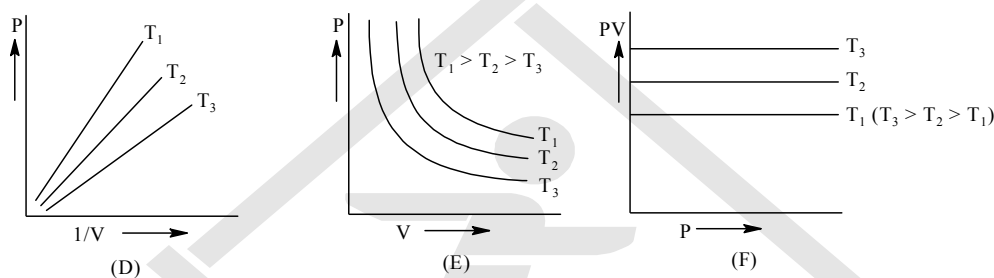
"Temperature remaining constant, the product of pressure and volume of a given mass of a gas is constant".

The value of the constant depends upon the amount of a gas and the temperature.

Mathematically, it can be written as,

$$P_1 V_1 = P_2 V_2 = P_3 V_3 = \dots\dots\dots$$

Location of straight line and curve changes with temperature in the **isotherm** shown in the following figure.



According to Boyle's law, $PV = \text{Constant}$ at constant temperature

$$\therefore \log P + \log V = \text{constant}$$

$$\log P = -\log V = \text{constant}$$

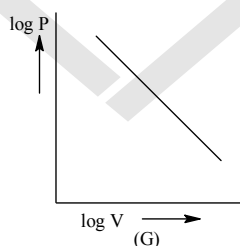


Illustration 1: A gas is present at a pressure of 2 atm. What should be the increase in pressure so that the volume of the gas can be decreased to $1/4^{\text{th}}$ of the initial value if the temperature is maintained constant.

Solution :

$PV = \text{constant}$ for a given mass of gas at constant temperature

$$\Rightarrow P_1 V_1 = P_2 V_2 \quad P_1 = 2 \text{ atm} \quad V_1 = V \quad V_2 = V/4 \quad P_2 = ?$$

$$\text{Now,} \quad 2 \times V = P_2 \times \frac{V}{4} \quad \Rightarrow \quad P_2 = 8 \text{ atm}$$

\therefore Pressure should be increased from 2 to 8 atm

\therefore total increase = $8 - 2 = 6 \text{ atm}$.

Illustration 2: A sample of gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmospheres? Assume that the temperature of the gas sample does not change.

Solution: Mass and temperature is constant hence we can use Boyle's law

$$P_1 V_1 = P_2 V_2$$

$$\text{Given } P_1 = 1 \text{ atm, } V_1 = 10 \text{ litre, } P_2 = 2 \text{ atm, } V_2 = ?$$

$$1 \times 10 = 2 \times V_2 \quad \Rightarrow \quad V_2 = 5 \text{ litre}$$

(ii) Charles' Law :

It relates the volume and temperature of a given mass of a gas at constant pressure.

For each degree change of temperature, the volume of a sample of a gas changes by the fraction $\frac{1}{273}$ of its volume at 0 °C.

Let the volume of a given amount of gas be V_0 at 0°C. The temperature is increased by $t^\circ\text{C}$ and the new volume becomes V_t

$$\text{Thus, } V_t = V_0 + \frac{V_0}{273} \times t = V_0 \left(1 + \frac{t}{273} \right) \text{ or } V_t = V_0 \left(\frac{273+t}{273} \right)$$

A new temperature scale was introduced known as Kelvin scale or absolute scale (named after the British physicist and mathematician Lord Kelvin). The lower limit of the scale is called absolute zero which corresponds to -273°C .

At absolute zero or -273°C , all molecular motions would stop and the volume of the gas would become zero. The gas would become a liquid or solid. Thus, absolute zero is that temperature at which no substance exists in the gaseous state. The temperature in absolute scale is always obtained by adding 273 to the temperature expressed in $^\circ\text{C}$.

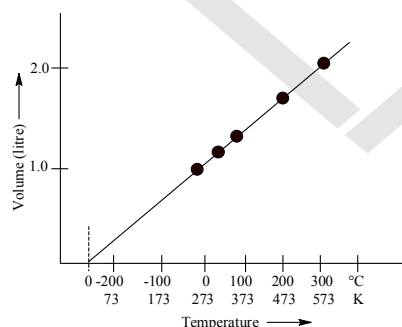
$$K = (t^\circ\text{C} + 273)$$

This new temperature scale may be used for deducing Charles' law.

By substituting T for $273 + t$ and T_0 for 273 in Eq. (i).

$$V_t = \frac{V_0 \times T}{T_0} \quad \text{or} \quad \frac{V_t}{T} = \frac{V_0}{T_0}$$

$$\text{or } \frac{V}{T} = \text{constant, if pressure is kept constant}$$



Alternatively, Charles' law can be stated as follows :

"The volume of a given amount of a gas at constant pressure varies directly as its absolute temperature".

$$V \propto T \quad (\text{if pressure is kept constant})$$

Illustration 3: 1 mole of an ideal gas at constant atmospheric pressure is heated to increase its volume by 50% of initial volume. The change in temperature made was 300 K to T K. Then calculate final temperature.

Solution : At constant pressure for a given amount of gas

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{V}{300} = \frac{1.5V}{T} \quad (V_1 = V, \quad T_1 = 300 \text{ K}, \quad V_2 = 1.5V)$$

$$T = 450 \text{ K}$$

(iii) Pressure-Temperature Law : (Gaylussac's Law)

It relates the pressure and absolute temperature of a given mass of a gas at constant volume.

Volumes remaining constant, the pressure of given mass of a gas increases or decreases by $\frac{1}{273}$ of its pressure at 0°C per degree change of temperature.

$$P_t = P_0 + \frac{P_0 \times t}{273} \quad \text{or} \quad P_t = P_0 \left(1 + \frac{t}{273}\right) \quad \text{or} \quad P_t = P_0 \left(\frac{273 + t}{273}\right) = P_0 \frac{T}{T_0}$$

$$\text{or} \quad \frac{P_t}{T} = \frac{P_0}{T_0} \quad \text{or} \quad P \propto T \quad (\text{if volume and number of moles are kept constant})$$

At constant volume, the pressure of a given amount of a gas is directly proportional to its absolute temperature.

Illustration 4: Pressure of gas contained in a closed vessel is increased by 0.4%, when heated by 1°C . Calculate its final temperature. Assume ideal nature.

Solution : Since no information is given about volume hence we can assume that volume is constant

$$\text{and use } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\text{given } P_1 = P, \quad T_1 = T, \quad P_2 = P + \frac{0.04P}{100} = 1.004P, \quad T_2 = T + 1$$

$$\therefore \frac{P}{T} = \frac{1.004P}{T+1} \Rightarrow T = 250 \text{ K}$$

(iv) Avogadro's Law

(i) For Solid, liquid and gas

1 mole of any substance contains Avogadro's number (N_A) of molecules/atoms/particles etc.

$$N_A = 6.023 \times 10^{23}$$

(ii) For gases:

In 1812, Amadeo Avogadro stated that samples of different gases which contain the same number of molecules (any complexity, size, shape) occupy the same volume at the same temperature and pressure. It follows from Avogadro's hypothesis that $V \propto n$ (T and P are constant).

$$V \propto n \quad (T, P \text{ constant}) \Rightarrow \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\begin{array}{ll} \text{STP : } 273.15 \text{ K} & 1 \text{ atm} \\ \text{SATP : } 298.15 \text{ K} & 1 \text{ bar} \end{array}$$

(v) Ideal Gas Equation

Combining all these gas laws, a simple equation can be derived at, which relates P , V , n and T for a gas

$$PV = nRT \quad (\text{for } n \text{ moles of gas})$$

$$\Rightarrow \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (\text{Combined gas law})$$

P is the pressure of the gas and can be expressed in atm or Pa . Correspondingly , the volume must be expressed in litres or m³ respectively. n is the number of moles and T is the temperature in Kelvin. R is called the universal gas constant.

Numerical Values of R

(i) In litre atmosphere = 0.0821 litre atm deg⁻¹ mole⁻¹

(ii) In ergs = 8.314 × 10⁷ erg deg⁻¹ mole⁻¹

(iii) In joules = 8.314 joules deg⁻¹ mol⁻¹

(iv) In calories = 1.937 cal deg⁻¹ mole⁻¹

Illustration 5 : An open vessel at 27°C is heated until 3/5th of the air in it has been expelled. Assuming that the volume of the vessel remains constant find

(A) the air escaped out if vessel is heated to 900K.

(B) temperature at which half of the air escapes out.

Solution : One should clearly note the fact that on heating a gas in a vessel, there are the number of moles of gas which go out, the volume of vessel remains constant.

Let initial no. of moles of gas at 300 K be 'n'. On heating 3/5 moles of air escape out at temperature T.

$$\therefore \text{Moles of air left at temperature } T = \left(n - \frac{3}{5}n \right) = \frac{2n}{5}$$

(A) On heating vessel to 900 K, let n₁ moles be left,

$$n_1 T_1 = n_2 T_2 \Rightarrow n_1 \times 900 = 300 \times n \Rightarrow n_1 = \frac{1}{3}n$$

$$\therefore \text{moles escaped out} = n - \frac{n}{3} = \frac{2}{3}n \text{ moles}$$

(B) Let n/2 moles escape out at temperature T, then

$$n_1 T_1 = n_2 T_2 \Rightarrow \frac{n}{2} \times T = n \times 300 \Rightarrow T = 600 \text{ K}$$

Illustration 6 : 5g of ethane is confined in a bulb of one litre capacity. The bulb is so weak that it will burst if the pressure exceeds 10 atm. At what temperature will the pressure of gas reach the bursting value?

Solution: $PV = nRT \Rightarrow 10 \times 1 = \frac{5}{30} \times 0.082 \times T$

$$T = \frac{60}{0.082} = 60 \times 12.18 = 730.81 \text{ K} = 457.81^\circ\text{C}$$

(vi) Relation between Molecular Mass and Gas Densities

(A) Actual density : For an ideal gas $PV = nRT$ or $PV = \frac{w}{M} RT$, where w = mass of the gas in gms and M = Molecular wt. in gms.

$$\therefore PM = \frac{w}{V} RT \quad \text{or} \quad PM = \rho RT, \text{ (where } \rho \text{ is the density of the gas} = \frac{w}{V} \text{)}$$

$$\therefore \rho = \frac{PM}{RT}$$

$$(i) \frac{d_1 T_1}{P_1} = \frac{d_2 T_2}{P_2} \quad (\text{for same gas at different temperature and pressure})$$

$$(ii) \frac{d_1}{d_2} = \frac{M_1}{M_2} \quad (\text{for different gases at same temperature \& pressure})$$

(Where d = density of gas)

Illustration 7: The density of an unknown gas at 98°C and 0.974 atm is $2.5 \times 10^{-3} \text{ g/ml}$. What is the mol wt. of gas?

Solution: Density = $2.5 \times 10^{-3} \text{ g/ml} = 2.5 \text{ g/L}$

$$\therefore PM = \rho RT$$

$$0.974 \times M = 2.5 \times 0.0821 \times 371 \quad \Rightarrow \quad M = 78.18.$$

(B) Vapour Density: For gases another term which is often used is vapour-density. Vapour density of a gas is defined as the ratio of the mass of the gas occupying a certain volume at a certain temperature and pressure to the mass of hydrogen occupying the same volume at the

same temperature and pressure i.e. $W(\text{gas}) = \frac{PVM}{RT}$.

$$\text{and } W_{\text{H}_2} = \frac{PV \times 2}{RT} \quad (\because \text{mol. wt. of hydrogen is } 2)$$

$$\therefore \frac{W_{\text{gas}}}{W_{\text{H}_2}} = \frac{M}{2} = (\text{Vapour density of gas})$$

Vapour density of a gas is same at any temperature, pressure and volume.

Illustration 8: When 3.2 g of sulphur is vapourised at 450°C and 723 mm pressure, the vapours occupy a volume of 780 ml . What is the molecular formula of sulphur vapours under these conditions? Calculate the vapour density also.

$$\text{Solution: } PV = nRT \Rightarrow \frac{723}{760} \times \frac{780}{760} = \frac{3.2}{M} \times 0.082 \times 723$$

$$M = 255.9$$

$$\text{no. of atoms of sulphur in one molecule} = \frac{M}{32} = 8$$

$$\therefore \text{Molecular formula of sulphur} = \text{S}_8$$

$$\text{V. D.} = \frac{M}{2} = \frac{255.9}{2} \Rightarrow 127.99$$

(vii) Dalton's Law of Partial Pressures:

The total pressure of a mixture of non-reacting gases is equal to the sum of their partial pressures.

$$\text{By Dalton's Law} \quad P_T = P_1 + P_2 + \dots$$

By the partial pressure of a gas in a mixture is meant, the pressure that the gas will exert if it occupies alone the total volume of the mixture at the same temperature.

Derivation: $n = n_1 + n_2 + \dots$

$$n = \frac{PV}{RT} \Rightarrow \frac{PV}{RT} = \frac{P_1V}{RT} + \frac{P_2V}{RT} + \dots \Rightarrow P = P_1 + P_2 + \dots$$

Assumption: Volume of all the gases is same as they are kept in same container.

Relationship between partial pressure and number of moles

Important formula

$$(i) \quad P_1 = \left(\frac{n_1}{n_1 + n_2} \right) P = x_1 P \quad \text{where } x_1 = \text{mole fraction of gas}$$

$$(ii) \quad \text{Partial pressure of a gas in the mixture} = \frac{\text{Volume of the gas}}{\text{Total Volume}} \times P$$

Partial pressure and aqueous tension: Dalton's law is used to calculate the pressure of a dry gas when it is collected over water at atmospheric pressure.

By Dalton's law,

Pressure of dry gas = atmospheric pressure - aqueous tension

Aqueous tension depends on temperature. It increases with temperature and becomes 760 mm at 100°C.

Illustration 9: A gaseous mixture contains 55% N_2 , 20% O_2 , and 25% CO_2 by mass at a total pressure of 760 mm. Calculate the partial pressure of each gas.

Solution:

Total mass of the gases = 100 g

$$W_{N_2} = 55g,$$

$$W_{O_2} = 20g,$$

$$W_{CO_2} = 25g$$

$$n_{N_2} = 55/28 = 1.964,$$

$$n_{O_2} = 20/32 = 0.625,$$

$$n_{CO_2} = 25/44 = 0.568$$

Total moles = 3.157

$$P_{N_2} = \frac{1.964 \times 760}{3.157} = 472.8 \text{ mm} \quad P_{O_2} = \frac{0.625 \times 760}{3.157} = 150.46 \text{ mm}$$

$$P_{CO_2} = \frac{0.568 \times 760}{3.157} = 136.74 \text{ mm}$$

Illustration 10: A mixture containing 1.6 g of O_2 , 1.4 g of N_2 and 0.4 g of He occupies a volume of 10 litre at 27°C. Calculate the total pressure of the mixture and partial pressure of each compound.

Solution:

$$PV = nRT$$

$$V = 10 \text{ litre}$$

$$T = 27^\circ\text{C} = 300\text{K}$$

$$n_{He} = \frac{0.4}{4} = 0.1, \quad n_{N_2} = \frac{1.4}{28} = 0.05, \quad n_{D_2} = \frac{1.6}{32} = 0.05$$

Total no. of moles = $0.1 + 0.05 + 0.05 \Rightarrow 0.2$

$$PV = nRT \Rightarrow P \times 10 = 0.2 \times 0.082 \times 300 = 0.04926 \Rightarrow P = 0.492 \text{ atm}$$

Partial pressure = Total pressure \times molefraction

$$P_{He} = 0.492 \times \frac{0.1}{0.2} = 0.246 \text{ atm}$$

$$P_{N_2} = 0.492 \times \frac{0.05}{0.2} = 0.123 \text{ atm}$$

$$P_{O_2} = 0.492 \times \frac{0.05}{0.2} = 0.123 \text{ atm}$$

(viii) Graham's Law of Diffusion

Diffusion is the tendency of any substance to spread throughout the space available to it. Diffusion will take place in all direction and even against gravity.

The streaming of gas molecules through a small hole is called effusion.

According to Graham, the rate of diffusion (or effusion) of a gas at constant pressure and temperature is inversely proportional to the square root of its molecular mass.

$$r \propto \sqrt{\frac{1}{M}}, \text{ at constant P and T}$$

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}, \text{ at constant P and T}$$

Since molecular mass of gas = $2 \times$ vapour density, $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$, at constant P and T

The rate of diffusion (or effusion) r of two gases under different pressure can be given by

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2} \text{ at constant T only.}$$

$$r = \frac{\text{Volume diffused (V)}}{\text{time taken}} = \frac{\text{moles diffused (n)}}{\text{time taken}}$$

$$r = \frac{\text{distance travelled in a narrow tube of uniform cross-sectional area (x)}}{\text{time taken}}$$

Therefore, according to Graham's law of diffusion (effusion) at constant P and T.

$$\frac{V_1}{t_1} \times \frac{t_2}{V_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

d_1 and d_2 are the respective densities and V_1 and V_2 are volumes diffused (effused) in time t_1 and t_2 .

$$\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

where n_1, n_2 are moles diffused (effused) in time t_1 and t_2 .

$$\frac{x_1}{t_1} \times \frac{t_2}{x_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

where x_1 and x_2 are distances travelled by molecules in narrow tube in time t_1 and t_2 .

$$\begin{aligned} r &= \frac{\text{moles diffused}}{\text{time taken}} \\ &= \frac{\text{distance travelled in a narrow tube}}{\text{time taken}} \\ &= \frac{\text{pressure drop I}}{\text{pressure drop II}} \end{aligned}$$

Note: It should be noted that the rate of diffusion or effusion actually depends on pressure difference of the gas and not simply on its pressure. Moreover the pressure difference is to be measured for this gas only i.e. if a container holds [He] at a pressure of 0.1 atm and if a small pin-hole is made in the container and if the container is placed in a room, then the rate of effusion of He gas from the container to outside depends only on its pressure difference, which is 0.1-0 (as there is no He in the atmosphere). This implies that the diffusion of a gas is not dependent on the diffusion of any other gas.

Whenever we consider the diffusion of gas under experimental conditions, we always assume that the gas diffuses in vacuum and during the time period for which the diffusion is studied the rate of diffusion (or the composition of diffusing or effusing mixture of gases) remains constant.

Illustration 11: Pure O_2 diffuses through an aperture in 224 seconds, whereas mixture of O_2 and another gas containing 80% O_2 diffuses from the same in 234 sec under similar condition of pressure and temperature. What is molecular wt. of gas?

Solution: The gaseous mixture contains 80% O_2 and 20% gas.

$$\therefore \text{Average molecular weight of mixture } (M_{\text{mix}}) = \frac{32 \times 80 + 20 \times m_{\text{mix}}}{100} \quad \dots (i)$$

Now for diffusion of gaseous mixture and pure O_2

$$\frac{r_{O_2}}{r_m} = \sqrt{\frac{M_{\text{mix}}}{M_{O_2}}} \quad \text{or} \quad \frac{V_{O_2}}{V_{\text{mix}}} \times \frac{t_{\text{mix}}}{t_{O_2}} = \sqrt{\frac{M_{\text{mix}}}{32}} \quad \text{or} \quad \frac{1}{224} \times \frac{234}{1} = \sqrt{\frac{M_{\text{mix}}}{32}} \quad \dots (ii)$$

$$\therefore M_{\text{mix}} = 34.92$$

By (i) and (ii) mol weight of gas (m) = 46.6.

Illustration 12: Calculate the relative rates of diffusion of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ in the gaseous state (Atomic mass of F = 19).

Solution $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ (at F = 19)

$$\begin{aligned} \frac{r_{\text{UF}_6^{235}}}{r_{\text{UF}_6^{238}}} &= \sqrt{\frac{M_{\text{UF}_6^{238}}}{M_{\text{UF}_6^{235}}}} \\ &= \sqrt{\frac{352}{349}} = 1.0042 \end{aligned}$$

4. The Kinetic Theory of Gases

In order to derive the theoretical aspect of the various gas laws based on simple experiment facts, Maxwell proposed the following postulates under the heading of kinetic theory of gases:

The postulates of kinetic theory of gas are

- (i) Each gas is made up of a large number of small (tiny) particles known as molecules.
- (ii) The volume of a molecule is so small that it may be neglected in comparison to total volume of gas.
- (iii) The molecules are never in stationary state but they are believed to be in chaotic (random) motion. They travel in straight line in all possible directions with altogether different but constant velocities. The direction of motion is changed by the collision with container or with the other molecules.
- (iv) The collision between molecules is perfectly elastic i.e., there is no change in the energies of the molecules after collision.
- (v) The effect of gravity on molecular motion is negligible.
- (vi) The kinetic energy of the gases depends on the temperature.
- (vii) The pressure of the gas arises due to collision of molecules with the walls of the container.

The Kinetic Equation : Maxwell also derived an equation on the basis of above assumptions as

$$PV = \frac{1}{3} mnu^2 \quad \text{where}$$

P	=	Pressure of gas
V	=	Volume of gas
m	=	mass of one molecule of gas
n	=	no. of molecules of gas
u	=	root mean square velocity of molecules

For 1 mole $n = N$ (Avogadro number)

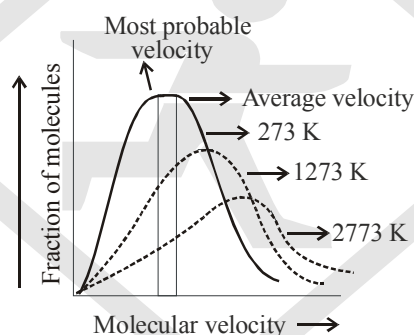
$m \times N = \text{Molecular mass } M.$

$$\therefore PV = \frac{1}{3} Mu^2 \quad \text{or} \quad u^2 = \frac{3PV}{M} = \frac{3RT}{M} \quad \text{or} \quad u = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}}$$

5. Distribution of Molecular Velocities

Maxwell and Boltzmann proposed that gas molecules are always in rapid random motion colliding with each other and with the walls of container. Due to such collisions, their velocities always changes. A fraction of molecules have a particular molecular velocity at a time. James Clark Maxwell calculated the distribution of velocity among fraction of total number of molecules, on the basis of probability.

The distribution of velocities of different gas molecules may be shown by the following curve.



From the curve it may be concluded that

- (i) Only a small fraction of molecules have either very low or very high velocity.
- (ii) Curve becomes flat when temperature is raised i.e. distribution around average velocity becomes wider. Average molecular velocity increases with rise in temperature.
- (iii) Most of the molecules have velocity close to most probable velocity represented by the top of curve.
- (iv) At higher temperature greater number of molecules have high velocity, while few molecules have lower velocity.

Average Velocity : As per kinetic theory of gases, each molecule is moving with altogether different velocity. Let 'n' molecules be present in a given mass of gas, each one moving with velocity $u_1, u_2, u_3, \dots, u_n$. The average velocity or U_{av} = average of all such velocity terms.

$$\text{Average velocity} = \frac{u_1 + u_2 + u_3 + \dots + u_n}{n}$$

$$U_{av} = \sqrt{\frac{8RT}{\pi M}}$$

Root Mean Square Velocity : Maxwell proposed the term U_{rms} as the square root of means of square of all such velocities.

$$U_{rms}^2 = \frac{u_1^2 + u_2^2 + u_3^2 + \dots}{n}$$

Also $U_{rms} = \sqrt{\frac{3RT}{M}}$

Most probable velocity: It is the velocity possessed by maximum no. of molecules.

$$U_{mpv} = \sqrt{\frac{2RT}{M}}$$

$$\begin{aligned} \text{Furthermore } U_{mpv} : U_{av} : U_{rms} &:: \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} \\ &= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1 : 1.128 : 1.224 \end{aligned}$$

Also $U_{av} = U_{rms} \times 0.9213$

Kinetic Energy of Gas: As per kinetic equation $PV = \frac{1}{3} mn u_{rms}^2$.

For 1 mole $m \times n = \text{Molecular Mass (M)}$

$$\therefore PV = \frac{1}{3} Mu_{rms}^2 = \frac{2}{3} \times \frac{1}{2} Mu^2 = \frac{2}{3} \times \text{K.E./mole} \quad \text{or} \quad \frac{\text{K.E.}}{\text{mole}} = \frac{3}{2} RT$$

$$\text{Also KE per molecule} = \frac{3}{2} \frac{RT}{n} = \frac{3}{2} kT. \text{ Where } k \text{ is the Boltzmann constant } \left(k = \frac{R}{n} \right)$$

Kinetic Energy of gas sample :

(i) Average kinetic energy of a single molecule $= \frac{3}{2} \cdot \frac{R}{N} \cdot T = \frac{3}{2} kT$

$k = \text{boltzman constant} = 1.38 \times 10^{-23} \text{ J/deg}$

(ii) Total Kinetic Energy for one mole of gas $= \frac{3}{2} RT$

(iii) kinetic Energy for n mol of gas $= n \times \frac{3}{2} RT$

Illustration 13: Calculate rms speed of O_2 at 273 K and 1×10^5 Pa pressure. The density of O_2 under these conditions is 1.42 kg m^{-3} .

Solution: Data are given in SI units

$$C = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 10^5}{1.42}} = 459.63 \text{ m sec}^{-1}$$

Illustration 14: At what temperature will the r.m.s. velocity of oxygen be one and half times of its value at N.T.P.?

Solution: $\frac{1}{2}mc^2 = \frac{3}{2}kT$

Suppose the temperature required is T' then the velocity will be $\frac{3}{2}C$

$$\therefore \frac{1}{2}mc'^2 = \frac{3}{2}kT' \quad \therefore \frac{3/2C}{C} = \sqrt{\frac{T'}{T}} \text{ or, } T' = \frac{9}{4} \times 273 = 614.25^\circ \text{ K}$$

Illustration 15: Calculate the average and total kinetic energy of 0.5 mole of an ideal gas at 0°C .

Solution: Average kinetic energy = $\frac{3}{2}KT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 273 = 5.65 \times 10^{-21} \text{ J}$

Total kinetic energy of n mole of gas = $n \times \frac{3}{2}RT = 0.5 \times \frac{3}{2} \times 8.314 \times 273$
= 1.702 kJ

6. Deviations from Ideal Behaviour

An ideal gas is one which obeys the gas laws of the gas equation $PV = RT$ at all pressure and temperatures. However no gas in nature is ideal. Almost all gases show significant deviations from the ideal behaviour. Thus the gases H_2 , N_2 and CO_2 which fail to obey the ideal-gas equation are termed as non-ideal or real gases.

Compressibility Factor : The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the compressibility factor, denoted by Z . It is defined as

$$Z = \frac{PV}{nRT}$$

The deviations from ideality may be shown by a plot of the compressibility factor Z , against P .

For an ideal gas, $Z = 1$ and it is independent of temperature and pressure.

The deviations from ideal behaviour of a real gas will be determined by the value of Z being greater or less than 1.

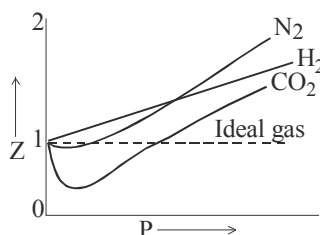
The difference between unity and the value of the compressibility factor of a gas is a measure of the degree of non ideality of the gas.

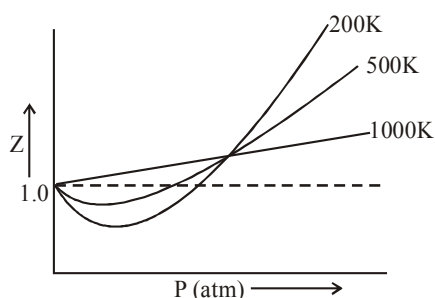
For a real gas, the deviations from ideal behaviour depends on :

- (i) pressure ; and (ii) temperature.

This will be illustrated by examining the compressibility curves of some gases discussed below with the variation of pressure and temperature.

Effect of Pressure Variation on Deviations:



Effect of Temperature on Deviations:

From the above curves we can conclude that:

1. At low pressure and fairly high temperatures, real gases show nearly ideal behaviour and the ideal-gas equation is obeyed.
2. At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal-gas equation is no longer valid.
3. The closer the gas is to the liquefaction point, the larger will be the deviation from the ideal behaviour.

Greater is the departure of Z from unity, more is the deviation from ideal behaviour.

- (i) When $Z < 1$, this implies that gas is more compressible.
- (ii) When $Z > 1$, this means that gas is less compressible.
- (iii) When $Z = 1$, the gas is ideal.

Vander Waals Equation of State for a Real Gas: The equation of state generated by Vander Waals in 1873 reproduces the observed behaviour with moderate accuracy. For n moles of gas, the Vander Waals equation is

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

where **a** and **b** are constants characteristic of a gas. This equation can be derived by considering a real gas and converting it to an ideal gas.

Volume Correction : We know that for an ideal gas $P \times V = nRT$. Now in a real gas the molecular volume cannot be ignored and therefore let us assume that '**b**' is the volume excluded (out of the volume of container) for the moving gas molecules per mole of a gas. Therefore due to n moles of a gas the volume excluded would be **nb**.

\therefore a real gas in a container of volume V has only available volume of $(V - nb)$ and this can be thought of, as an ideal gas in a container of volume $(V - nb)$

Pressure Correction : Let us assume that the real gas exerts a pressure P . The molecules that exert the force on the container will get attracted by molecules of the immediate layer which are not assumed to be exerting pressure.

It can be seen that pressure the real gas exerts would be less than the pressure an ideal gas would have exerted. Therefore if a real gas exerts a pressure P , then an ideal gas would exert a pressure equal to $P + p$ (p is the pressure lost by the gas molecules due to attractions). This small pressure p would be directly proportional to the extent of attraction between the molecules which are hitting the container wall and the molecules which are attracting these.

Therefore $p \propto \frac{n}{V}$ (concentration of molecules which are hitting the container's wall)

$p \propto \frac{n}{V}$ (concentration of molecules which are attracting these molecules) $\Rightarrow p \propto \frac{n^2}{V^2}$

$$\therefore p = \frac{an^2}{V^2}$$

where **a** is the constant of proportionality which depends on the nature of gas. Higher value of 'a' reflects the increased attraction between gas molecules.

The Vander Waals constant **b** (the excluded volume) is actually 4 times the volume of a single molecule. i.e. **b = 4 N_AV** where N_A → Avogadro number.

$$\therefore b = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \pi r^3, \text{ where } r \text{ is the radius of a molecule.}$$

The constant a and b: Vander Waals constant for attraction (A) and volume (B) are characteristic for a given gas. Some salient features of 'a' and 'b' are:

- (i) For a given gas Vander Waal's constant of attraction 'a' is always greater than Vander Waals constant of volume (B).
- (ii) The gas having higher value of 'a' can be liquified easily and therefore H₂ and He are not liquified easily.
- (iii) The units of a = litre² atm mole⁻² and that of b = litre mole⁻¹
- (iv) The numerical values of a and b are in the order of 10⁻¹ to 10⁻² to 10⁻⁴ respectively.
- (v) Higher is the value of 'a' for a given gas, easier is the liquification.

Explanation of deviation by Van der Waals equation

- (i) **At lower pressure :** 'V' is large and 'b' is negligible in comparison with V. Then Vander Waals equation reduces to :

$$\left(P + \frac{a}{V^2}\right)V = RT \Rightarrow PV + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V} \Rightarrow Z = \frac{PV}{RT} = 1 - \frac{a}{VRT}$$

or **PV < RT** at low pressure (below Boyle temperature)
this accounts for the dip in PV vs P isotherm at low pressure.

- (ii) **At fairly high pressures :** $\frac{a}{V^2}$ may be neglected in comparison with P.

The Vander Waals equation becomes

$$P(V-b) = RT \Rightarrow PV - Pb = RT$$

$$PV = RT + Pb \Rightarrow Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

or **PV > RT** at higher pressure (above Boyle temperature)

This accounts for the rising parts of the PV vs P isotherm at high pressures.

- (iii) **At very low pressure :** V becomes so large that both b and $\frac{a}{V^2}$ become negligible and the Vander Waals equation reduces to **PV = RT**

$$Z = \frac{PV}{RT} = 1 ; Pb = \frac{a}{V} \text{ At extremely low pressure (at Boyle temperature)}$$

This shows why gases approach ideal behaviour at very low pressures.

- (iv) **Hydrogen and Helium :** These are two lightest gases known. Their molecules have very small masses. The attractive forces between such molecules will be extensively small. So

$\frac{a}{V^2}$ is negligible even at ordinary temperatures. Thus **PV > RT**.

Dieterici Equation :

$$P(V - nb) = nRT e^{a/VRT} \quad (\text{for 'n' mole of a gas})$$

Berthelot Equation :

$$\left(P + \frac{n^2 a}{TV^2} \right) (V - nb) = nRT$$

Virial Equation Of State For 1 Mole Of Gas :

$$Z = \frac{PV}{RT} = 1 + B \frac{1}{V} + C \frac{1}{V^2} + D \frac{1}{V^3} + \dots$$

$$B = \text{second virial co-efficient, temperature dependent} = b - \frac{a}{RT}$$

$$C = \text{third virial co-efficient, temperature dependent} = b^2$$

Illustration 16 : The compressibility factor for 1 mole of a van der Waals gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant, *a*.

Solution:

For 1 mole of the gas,

$$Z = \frac{pV}{RT} \Rightarrow 0.5 = \frac{100 \times V}{.0821 \times 273}; V = 0.112 \text{ L}$$

$$\text{Neglecting } b, \text{ van der Waals equation reduces to } \left(P + \frac{a}{V^2} \right) V = RT$$

$$\text{or } pV + \frac{a}{V} = RT$$

$$\text{or } 100 \times 0.112 + \frac{a}{0.112} = .0821 \times 273$$

$$a = 1.25 \text{ L}^2\text{atm mol}^{-2}$$

7. Critical phenomenon & Liquification of gases

The phenomena of converting a gas into liquid is known as liquifaction. The liquifaction of gas is achieved by controlling P and T as follows:

1. **Increasing pressure** : An increase in pressure results in an increase in attraction among molecules.
2. **Decreasing temperature** : A decrease in temperature results in decrease in kinetic energy of molecules.

Critical temperature (T_c) : It is defined as the characteristic temperature for a given gas below which a continuous increase in pressure will bring liquification of gas and above which no liquefaction is noticed although pressure may be increased e.g. T_c for CO_2 is 31.2°C .

$$T_c = \frac{8a}{27Rb}$$

Critical pressure (P_c) : It is defined as the minimum pressure applied on 1 mole of gas placed at critical temperature, to just liquefy the gas

$$P_c = \frac{a}{27b^2}$$

Critical Volume (V_c) : The volume occupied by 1 mole of gas placed at critical conditions.

$$V_c = 3b \text{ (i.e. } P = P_c \text{ and } T = T_c \text{)}$$

8. Collision parameters

– Mean free path

$$\lambda = \frac{d_1 + d_2 + \dots + d_n}{n} = \eta \sqrt{\frac{3}{Pd}} \quad (\eta = \text{coefficient of viscosity})$$

$$\lambda = \frac{\text{Average velocity / RMS velocity}}{\text{collision number or frequency}} = \frac{kT}{\sqrt{2} \pi \sigma^2 P}$$

k = Boltzman constant ; σ = collision diameter.

– Collision frequency (z)

 : no. of collision taking place per second per unit volume.

– Collision diameter

 : Closest distance between the centre of two molecule which are participating in collision.

– Relative Humidity (RH) :

At a given temperature

$$RH = \frac{\text{Partial pressure of water vapour in air at } T}{\text{vapour pressure of water at } T}$$

– Loschmidt Number

The number of molecules present in 1 cc of gas (or) vapour at STP.

value : 2.617×10^{19} 1 cc

SOLVED EXAMPLES

Ex.1 When 2 gm of a gaseous substance A is introduced into an initially evacuated flask at 25°C, the pressure is found to be 1 atm. 3 gm another gaseous substance B is then added to it at the same temperature and pressure. The final pressure is found to be 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights of A and B.

Sol. Let M_A and M_B be the molecular weights of A and B.

Using $PV = nRT$ for A, we get :

$$1 = \frac{\frac{2}{M_A} RT}{V} \quad \dots(i)$$

and using Dalton's Law : $P_{\text{Total}} = \frac{(n_A + n_B)RT}{V} \Rightarrow 1.5 = \frac{\left(\frac{2}{M_A} + \frac{3}{M_B}\right)RT}{V} \quad \dots(ii)$

Solving (i) and (ii), we get $\frac{M_A}{M_B} = \frac{1}{3}$

Ex.2 Which of the two gases, ammonia and hydrogen chloride, will diffuse faster and by what factor ?

Sol. By Graham's Law :

$$\frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}} = \sqrt{\frac{36.5}{17}} \approx 1.46 \Rightarrow r_{\text{NH}_3} = 1.46 r_{\text{HCl}}$$

Thus, ammonia will diffuse 1.46 times faster than hydrogen chloride gas.

Ex.3 The ratio of rate of diffusion of gases A and B is 1 : 4 and their molar mass ratio is 2 : 3. Calculate the composition of the gas mixture initially effusing out.

Sol. By Graham's Law :

$$\frac{r_A}{r_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} \Rightarrow \frac{1}{4} = \frac{P_A}{P_B} \sqrt{\frac{3}{2}} \Rightarrow \frac{P_A}{P_B} = \frac{1}{4} \sqrt{\frac{2}{3}}$$

$$\Rightarrow \text{Mole ratio of gas A and B effusing out} = \frac{1}{4} \sqrt{\frac{2}{3}} \quad [\text{moles} \propto \text{pressure}]$$

Ex.4 At 30°C and 720 mm of Hg, the density of a gas is 1.5 g/lit. Calculate molecular mass of the gas. Also find the number of molecules in 1 cc of the gas at the same temperature.

Sol. Assuming ideal behaviour and applying ideal gas equation :

$$PV = nRT$$

Another form of gas equation is $PM_0 = dRT$

$$\Rightarrow M_0 = \frac{dRT}{T} = \frac{1.5 \times 0.0821 \times 303}{720/760} \quad (T = 30 + 273 \text{ K})$$

$$\Rightarrow M_0 = 39.38$$

Now number of molecules = $n \times N_0$

$$= \frac{PV}{RT} \times N_0 = \frac{720/760 \times 1 \times 10^{-3}}{0.0821 \times 303} \times 6.023 \times 10^{23}$$

$$= 2.29 \times 10^{19}$$

Ex.5 The pressure exerted by 12 gm of an ideal gas at temperature $t^\circ\text{C}$ in a vessel of volume V litre is one atm. When the temperature is increased by 10° at the same volume, the pressure rises by 10% calculate the temperature t and volume V . (molecular mass of the gas = 120 gm/mole)

Sol. Using Gas equation : $PV = nRT$

$$\text{We have,} \quad P \times V = 0.1 \times R \times t \quad \dots(1)$$

$$\text{and} \quad 1.1 P \times V = 0.1 \times R \times (t + 10) \quad \dots(2)$$

$$\text{Using (i) and (ii), we have : } \frac{t}{t+10} = \frac{1}{1.1}$$

$$\Rightarrow t = 100 \text{ K or } t = -173^\circ\text{C}$$

Putting the value of t in (i), we get :

$$\Rightarrow 1 \times V = 0.1 \times 0.0821 \times 100 \Rightarrow V = 0.821 \text{ L}$$

Ex.6 Assuming that the air is essentially a mixture of nitrogen and oxygen in mole ratio of 4 : 1 by volume. Calculate the partial pressures of N_2 and O_2 on a day when the atmospheric pressure is 750 mm of Hg. Neglect the pressure of other gases.

Sol. From Dalton's Law of partial pressure, we have

$$\text{Partial pressure of nitrogen} = p_{N_2} = \chi_{N_2} \times P \text{ and Partial pressure of oxygen} = p_{O_2} = \chi_{O_2} \times P$$

Now, $\chi_{N_2} = 4/5$, and $\chi_{O_2} = 1/5$

$$\Rightarrow p_{N_2} = \frac{4}{5} \times 750 = 600 \text{ mm of Hg and } p_{O_2} = \frac{1}{5} \times 750 = 150 \text{ mm of Hg}$$

Ex.7 *An open vessel at 27°C is heated until three fifth of the air has been expelled, Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated.*

Sol. In the given questions, volume is constant. Also, as the vessel is open to atmosphere, the pressure is constant. This means that the gas equation is simply reduced to the following form :

$$nT = \text{constant (Use } PV = nRT)$$

$$\text{or } n_1 T_1 = n_2 T_2$$

Now let n_1 = initial moles and n_2 = final moles

$$\Rightarrow n_2 = 2/5 \times n_1 \text{ (as 3/5th of the air has been expelled)}$$

$$\Rightarrow T_2 = \frac{n_1 T_1}{n_2} = \frac{n_1 T_1}{2/5 n_1} = \frac{5}{2} T_1$$

$$\Rightarrow T_2 = \frac{5}{2} (300) = 750 \text{ K} = 477^\circ\text{C}$$

Ex.8 *When 3.2 gm of sulphur is vaporized at 450° C and 723 mm pressure, the vapour occupies a volume of 780 m, what is the formula for the sulphur under these conditions ?*

Sol. The molecular weight = no. of atoms \times atomic mass

So let us find the molecular weight of S from the data given.

$$M_0 = \frac{gRT}{PV} = \frac{3.2 \times 0.082 \times 723}{(723 \times 760) \times (780/1000)} = 256$$

$$\Rightarrow \text{Number of atoms} = \frac{256}{32} = 8$$

Hence, molecular formula of sulphur = S_8

Ex.9 *A spherical balloon of 21 cm diameter is to be filled with H_2 at NTP from a cylinder containing the gas at 20 atm at 27°C. If the cylinder can hold 2.80L of water, calculate the number of balloons that can be filled up.*

Sol. The capacity of cylinder = 2.80 L

Let n = moles of hydrogen contained in cylinder and n_0 = moles of hydrogen required to fill one balloon.

$$n = \frac{PV}{RT} = \frac{20 \times 280}{0.0821 \times 300} = 2.273$$

$$n_0 = \frac{\text{volume of balloon}}{22400} \quad (\text{Note : the balloons are being filled at S.T.P.})$$

$$= \frac{4/3 \pi r^2}{22400} = \frac{4/3 \times 3.14 \times (10.5)^3}{22400} = 0.2164$$

$$\Rightarrow \text{Number of balloons that can be filled} = \frac{n}{n_0} = 10.50 \approx 10$$

Ex.10 A mixture containing 1.12L of H_2 and 1.12L of D_2 (deuterium) at S.T.P. is taken inside a bulb connected to another bulb by a stop-cock with a small opening. The second bulb is fully evacuated; the stop-cock is opened for a certain time and then closed. The first bulb is found to contain 0.05 gm of H_2 . Determine the % age composition by weight of the gases in the second bulb.

Sol. In the first bulb :

$$\text{Initial moles of } H_2 = 1.12 / 22.4 = 1/20$$

$$\text{Initial moles of } D_2 = 1.12/22.4 = 1/20$$

Now after opening of stop-cock, mass of H_2 left in the first bulb = 0.05

$$\Rightarrow \text{Moles of } H_2 = 0.05/2 = 1/40$$

$$\Rightarrow \text{Moles of } H_2 \text{ effused into second bulb} = 1/20 - 1/40 = 1/40$$

Let n be number of moles of D_2 effused.

From Graham's Law :

$$\frac{n}{1/40} = \sqrt{\frac{2}{4}}$$

$$\Rightarrow n = \frac{\sqrt{2}}{80} = \text{moles of } D_2 \text{ in second bulb.}$$

In the second bulb :

$$\text{The mass of } H_2 \text{ gas} = 1/40 \times 2 = 0.05 \text{ gm}$$

$$\text{The mass of } D_2 \text{ gas} = \sqrt{2}/80 \times 4 = 0.07 \text{ gm}$$

- \Rightarrow Total mass = $0.05 + 0.07 = 0.12$ gm
 \Rightarrow % of $H_2 = 0.05/1.12 \times 100 = 41.67$ %
 \Rightarrow % of $D_2 = 0.07/1.12 \times 100 = 58.13$ %

Ex.11 The pressure in a bulb dropped from 2000 mm to 1500 mm of Hg in 47 min when the contained O_2 leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas (B) of molecular weight 79 in the molar ratio of 1 : 1 at a total pressure of 4000 mm of Hg was introduced. Find the molar ratio of the two gases remaining in the bulb after a period of 74 min.

Sol. Now as $P \propto n$ (moles), we define the rate of diffusion as the drop in the pressure per second. First we try to find the rate of diffusion of the gas B.

The rate of diffusion of $O_2 = R_0 = (2000 - 1500)/47 = 10.638$ mm/min.

Assuming that gas B was present alone in the bulb. Let the rate of diffusion of B = R_B .

From Graham's Law of diffusion, we have :

$$\frac{R_B}{R_0} = \sqrt{\frac{M_{O_2}}{M_B}} = \sqrt{\frac{32}{79}} = 0.636$$

$$\Rightarrow R_B = 10.638 \times 0.636 = 6.77 \text{ mm/min}$$

Now the bulb contains mixture of O_2 and B in the mole ratio of 1 : 1 at total pressure of 4000 mm Hg.

$$\Rightarrow P_{O_2} = P_B = 2000 \text{ mm of Hg}$$

As the pressure and temperature conditions are same for both gases in the second case (same bulb), so the rate of diffusion will remain same in the second case also.

Let X_0 and X_B be the final pressure in the bulb after leakage for 74 minutes.

$$R_0 = \frac{2000 - X_0}{74} = 10.638$$

$$\Rightarrow X_0 = 1212.78$$

$$R_B = \frac{2000 - X_B}{74} = 6.77 \Rightarrow X_B = 1498.96$$

As $P \propto n$

$$\Rightarrow \text{Ratio of moles is given as : } X_0 : X_B = 1 : 1235$$

Ex.12 A 672 ml of a mixture of oxygen-ozone at N.T.P. were found to be weigh 1 gm. Calculate the volume of ozone in the mixture.

Sol. Let V ml of ozone are there in the mixture

$$\Rightarrow (672 - V) \text{ m; } = \text{vol. of oxygen}$$

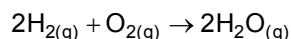
$$\text{Mass of ozone at N.T.P.} = \frac{V}{22400} \times 48$$

$$\text{Mass of oxygen at N.T.P.} = \frac{672 - V}{22400} \times 32$$

$$\Rightarrow \frac{V}{22400} \times 48 + \frac{672 - V}{22400} \times 32 = 1 \quad \Rightarrow \quad \text{On solving we get: } V = 56 \text{ ml}$$

Ex.13 A 20 L flask contains 4.0 gm of O_2 & 0.6 gm of H_2 at 100°C . If the contents are allowed to react to form water vapors at 100°C , find the contents of flask and there partial pressures.

Sol. H_2 reacts with O_2 to form water [$\text{H}_2\text{O}_{(g)}$]



$$\Rightarrow 2 \text{ moles of } \text{H}_2 = 1 \text{ mole of } \text{O}_2 = 2 \text{ moles of } \text{H}_2\text{O}$$

Here masses of H_2 and O_2 are given, so one of them can be in excess. So first check out which of the reactants is in excess.

$$\text{Now, Moles of } \text{O}_2 = 4/32 = 0.125 \text{ and Moles of } \text{H}_2 = 0.6/2 = 0.3$$

$$\text{Since } 1 \text{ mole of } \text{O}_2 \equiv 2 \text{ moles of } \text{H}_2$$

$$\Rightarrow 0.125 \text{ moles of } \text{O}_2 \equiv 2 \times 0.125 \text{ moles of } \text{H}_2$$

i.e. 0.25 moles of H_2 are used, so O_2 reacts completely whereas H_2 is in excess.

$$\Rightarrow \text{Moles of } \text{H}_2 \text{ in excess} = 0.3 - 0.25 = 0.05 \text{ moles.}$$

$$\text{Also, } 2 \text{ moles of } \text{H}_2 \equiv 2 \text{ moles of } \text{H}_2\text{O}$$

$$\Rightarrow 0.25 \text{ moles of } \text{H}_2 \equiv 0.25 \text{ moles of } \text{H}_2\text{O} \text{ are produced.}$$

$$\Rightarrow \text{Total moles after the reaction} = 0.05 \text{ (moles of } \text{H}_2) + 0.25 \text{ (moles of } \text{H}_2\text{O}) = 0.3$$

$$\Rightarrow \text{The total pressure } P_{\text{Total}} \text{ at the end of reaction is given by :}$$

$$P_{\text{Total}} = \frac{nRT}{V} = \frac{0.3 \times 0.0821 \times 373}{20} = 0.459 \text{ atm}$$

$$\text{Now partial pressure of A} = \text{mole fraction of A} \times P_{\text{Total}}$$

$$\Rightarrow P_{\text{H}_2} = 0.05/0.3 \times 0.459 = 0.076 \text{ atm}$$

$$\Rightarrow P_{\text{H}_2\text{O}} = 0.25/0.3 \times 0.459 = 0.383 \text{ atm}$$

Ex.14 The compressibility factor for 1 mole of a van Waals gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecular is negligible, calculate the van der Waals constant 'a'.

Using van der Waal's equation of state :

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\text{Now : } V - nb \approx V(\text{given})$$

$$\Rightarrow \text{The equation is reduced to : } \left(P + \frac{a}{V^2}\right)V = RT$$

$$\text{or } Z = \frac{PV}{RT} = \frac{V}{RT} \left(\frac{RT}{V} - \frac{a}{V^2}\right) = 1 - \frac{a}{RTV}$$

$$0.5 = \frac{100 \times V}{0.0821 \times 273} \Rightarrow V = 0.112 \text{ L}$$

$$\text{Also, } 0.5 = 1 - \frac{a}{RTV}$$

Substitute the values of V and T :

$$\Rightarrow a = 1.25 \text{ litre}^2 \text{ mol}^{-2} \text{ atm.}$$

Ex.15 Calculate the pressure exerted by 5 mole of CO₂ in one litre vessel at 47°C using van der waals equation. Also report the pressure of gas if it behaves ideally in nature.

(a = 3.592 atm litre² mol⁻², b = 0.0427 litre mol⁻¹)

Using van der waals equation of state :

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\text{Substituting the given values, we get : } \left(P + \frac{3.592 \times 5^2}{1^2}\right)(1 - 5 \times 0.0427) = 5 \times 0.0821 \times 320$$

$$\Rightarrow P = 77.218 \text{ atm}$$

If the gas behaves ideally, then using : $PV = nRT$

$$\Rightarrow P = \frac{5 \times 0.0821 \times 320}{1} \text{ atm} = 131.36 \text{ atm}$$

SOLVED EXAMPLES**IIT-JEE MAINS**

Ex.1 A gas occupies 300 ml at 27°C and 730 mm pressure. What would be its volume at STP-

- (A) 162.2 ml (B) 262.2 ml (C) 362.2 ml (D) 462.2 ml

Sol. (B)

Given at $T_1 = 300$ K, $T_2 = 273$ K (STP)

$$V_1 = 300 \text{ ml} = \left(\frac{300}{1000}\right) \text{ litre}, P_1 = \left(\frac{730}{760}\right) \text{ atm. } P_2 = 1 \text{ atm.}, V_2 = ?$$

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2},$$

$$\frac{730 \times 300}{760 \times 1000 \times 300} = \frac{1 \times V_2}{273}$$

$$\therefore V_2 = 0.2622 \text{ litre} = 262.2 \text{ ml.}$$

Ex.2 A truck carrying oxygen cylinders is filled with oxygen at -23°C and at a pressure of 3 atmosphere in Srinagar, Kashmir. Determine the internal pressure when the truck drives through Madras. Tamilnadu. Where the temperature is 30°C -

- (A) 2.64 atm. (B) 1.64 atm. (C) 1 atm. (D) 3.64 atm.

Sol. (D)

$$P_1 = 3 \text{ atm.}, P_2 = ?$$

$$T_1 = -23 + 273 = 250 \text{ K}$$

$$T_2 = 273 + 30 = 303 \text{ K.}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2},$$

$$\frac{3}{250} = \frac{P_2}{303}$$

$$P_2 = \frac{3 \times 303}{250} = 3.64 \text{ atm.}$$

Ex.3 The density of a gas at -23°C and 780 torr is 1.40 gram per litre. Which one of the following gases is it -

- (A) CO₂ (B) SO₂ (C) Cl₂ (D) N₂

Sol. (D)

$$PV = nRT$$

$$\frac{780}{760} \times 1 = n \times .082 \times (273 - 23)$$

$$n = \frac{780}{760 \times 0.082 \times 250}$$

$n = 0.0501$ moles.

$\therefore .0501$ moles of the gas weigh = 1.40 gm.

$\therefore 1$ mole of gas weigh = $\frac{1.40}{.0501} = 28$ gram.

So gas is N_2 .

- Ex. 4** Calculate the weight of CH_4 in a 9 litre cylinder at 16 atm and $27^\circ C$ ($R = 0.08$ lit. atm/K) -
 (A) 96 gm (B) 86 gm (C) 80 gm (D) 90 gm

Sol. (A)

Given $P = 16$ atm, $V = 9$ litre.

$T = 300$ K, $m_{CH_4} = 16$, $R = 0.08$ litre atm/k.

$PV = w/m \times R \times T$

$$16 \times 9 = \frac{w}{16} \times 0.08 \times 300$$

$w = 96$ gm.

- Ex. 5** What is the density of sulphur dioxide (SO_2) at STP -
 (A) 2.86 gm/lit. (B) 1.76 gm/lit (C) 1.86 gm/lit (D) None of these.

Sol. (A)

The gram molecular weight of $SO_2 = 64$ gm/mole.

Since 1 mole of SO_2 occupies a volume of 22.4 litres at S.T.P.

Density of $SO_2 = \frac{64}{22.4} = 2.86$ gm/lit.

- Ex.6** 5gm of XeF_4 gas was introduced into a vessel of 6 litre capacity at $80^\circ C$. What is the pressure of the gas in atmosphere -
 (A) .21 atm (B) .31 atm (C) .11 atm (D) .41 atm.

Sol. (C)

Given $V = 6$ litre, $T = 353$ K, $R = 0.082$, $W = 5$ gm. $m = 207.3$

$$PV = \frac{W}{m} \times R \times T$$

$$P \times 6 = \frac{5}{207.3} \times 0.082 \times (273 + 80)$$

$$P = \frac{5 \times 0.082 \times 353}{6 \times 207.3} = .11 \text{ atm.}$$

- Ex.7** Calculate the temperature at which 28 gm N_2 occupies a volume of 10 litre at 2.46 atm-
 (A) 300 K (B) 320 K (C) 340 K (D) 280 K

Sol. (A)

Given $w_{N_2} = 28$ gm ,

$P = 2.46$ atm, $V = 10$ litre. $m_{N_2} = 28$,

$$\therefore PV = \left(\frac{w}{m}\right)RT$$

$$2.46 \times 10 = \left(\frac{28}{28}\right) \times 0.0821 \times T$$

$$T = 300 \text{ K.}$$

Ex.8 A mixture of gases at 760 mm pressure contains 65% nitrogen, 15% oxygen and 20% Carbondioxide by volume. What is the partial pressure of each in mm -

(A) 494, 114, 252

(B) 494, 224, 152

(C) 494, 114, 152

(D) None of these.

Sol. (C)

$$P'_{N_2} = 760 \times \frac{65}{100} = 494 \text{ mm}$$

$$P'_{O_2} = 760 \times \frac{15}{100} = 114 \text{ mm}$$

$$P'_{CO_2} = 760 \times \frac{20}{100} = 152 \text{ mm.}$$

Ex.9 0.45 gm of a gas 1 of molecular weight 60 and 0.22 gm of a gas 2 of molecular weight 44 exert a total pressure of 75cm of mercury. Calculate the partial pressure of the gas 2 -

(A) 30 cm of Hg

(B) 20 cm of Hg

(C) 10 cm of Hg

(D) 40 cm of Hg.

Sol. (A)

$$\begin{aligned} \text{No. of moles of gas 1} = n_1 &= \frac{w_1}{m_1} = \frac{0.45}{60} \\ &= 0.0075 \end{aligned}$$

$$\begin{aligned} \text{No. of moles of gas 2} = n_2 &= \frac{w_2}{m_2} = \frac{0.22}{44} \\ &= 0.0050 \end{aligned}$$

$$\begin{aligned} \text{Total no. of moles} &= n_1 + n_2 \\ &= 0.0075 + 0.0050 = 0.0125 \end{aligned}$$

$$P_2 \text{ partial pressure of gas 2} = \frac{0.0050}{0.0125} \times 75 = 30 \text{ cm of Hg.}$$

Ex. 10 The total pressure of a sample of methane collected over water is 735 torr at 29°C. The aqueous tension at 29°C is 30 torr. What is the pressure exerted by dry methane -

(A) 605 torr

(B) 205 torr

(C) 405 torr

(D) 705 torr

Sol. (D)

$$P_{\text{total}} = P_{\text{dry methane}} + P_{\text{water}}$$

$$735 = P_{\text{dry methane}} + 30$$

$$\therefore P_{\text{dry methane}} = 735 - 30 = 705 \text{ torr.}$$

Ex.11 The odour from a gas A takes six seconds to reach a wall from a given point. If the molecular weight of gas A is 46 grams per mole and the molecular weight of gas B is 64 grams per mole. How long will it take for the odour from gas B to reach the same wall from the same point. Approximately -

- (A) 6 Sec (B) 7 Sec (C) 8 Sec (D) 9 Sec

Sol. (B)

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{r_A}{r_B} = \sqrt{\frac{64}{46}} = 1.18$$

Time taken for the odour of B to reach the wall = $1.18 \times 6 = 7.08 \text{ sec} \cong 7 \text{ sec}$.

Ex.12 1 litre of oxygen effuses through a small hole in 60 min. and a litre of helium at the same temperature and pressure effuses through the same hole in 21.2 min. What is the atomic weight of Helium -

- (A) 2.99 (B) 3.99 (C) 2.08 (D) 1.99

Sol. (B)

$$\frac{r_{O_2}}{r_{He}} = \frac{1000/60}{1000/21.2} = \frac{21.2}{60} = \sqrt{\frac{M_{He}}{M_{O_2}}}$$

$$= \sqrt{\frac{M_{He}}{32}}$$

$$\text{Squaring both of sides} = \frac{(21.2)^2}{(60)^2} = \frac{M_{He}}{32} \quad M_{He} = \frac{(21.2)^2 \times 32}{(60)^2} = 3.99$$

Since Helium is monoatomic so

Atomic weight = Molecular weight = 3.99

Ex.13 What is the temperature at which oxygen molecules have the same r.m.s. velocity as the hydrogen molecules at 27°C -

- (A) 3527°C (B) 4227°C (C) 4527°C (D) 4000°C

Sol. (C)

$$\text{r.m.s. velocity } C = \sqrt{\frac{3RT}{M}}$$

$$\text{For oxygen } Co_2 = \sqrt{\frac{3RT}{32}}$$

$$\text{For } CH_2 \text{ at } 27^\circ C = \sqrt{\frac{3 \times R \times 300}{2}}$$

When $Co_2 = CH_2$

$$\sqrt{\frac{3RT}{32}} = \sqrt{\frac{3 \times R \times 300}{2}}$$

$$\frac{3RT}{32} = \frac{3R \times 300}{2}$$

$$T = \frac{300 \times 32}{2} = 4800 \text{ K.}$$

$$\text{Then in } ^\circ\text{C } T = 4800 - 273 = 4527^\circ\text{C}$$

Ex.14 Calculate the total kinetic energy in joules, of the molecules in 8 gm of methane at 27°C -

- (A) 1770.5 Joule (B) 1870.5 joule (C) 1970.5 joule (D) 1670.5 joule

Sol. (B)

$$E_K (\text{For 1 mole}) = \frac{3}{2} RT = 3741 \text{ Joule.}$$

Total energy of 8 gm of methane

$$= \frac{1}{2} \text{ mole of methane}$$

$$= \frac{3741}{2} = 1870.5 \text{ Joule.}$$

Ex.15 Calculate the root mean square velocity of SO_2 at S.T.P. -

- (A) $3.26 \times 10^4 \text{ cm/sec}$ (B) $1.26 \times 10^2 \text{ cm/sec}$
 (C) $1.26 \times 10^4 \text{ cm/sec}$ (D) $3.26 \times 10^2 \text{ cm/sec}$

Sol. (A)

$$\therefore v_{\text{rms}} \text{ of } \text{SO}_2 = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 273}{64}} = 3.26 \times 10^4 \text{ cm/sec.}$$

Ex.16 Calculate the number of atoms in 1 g of helium

- (A) 1.506×10^{23} atoms (B) 1.605×10^{32} atoms
 (C) 1.056×10^{25} atoms (D) None of these

Sol. (A)

Atomic mass of He = 4

4 g of He contain = 6.023×10^{23} atoms

1 g of He contains =

$$\frac{6.023 \times 10^{23}}{4} = 1.506 \times 10^{23} \text{ atoms.}$$

Ex.17 7.00 g. of a gas occupies a volume of 4.1 litres at 300 K and 1 atmosphere pressure. Calculate the molecular mass of the gas -

- (A) 40 g mol^{-1} (B) 42 g mol^{-1} (C) 48 g mol^{-1} (D) 45 g mol^{-1}

Sol. (B)

$$PV = nRT$$

$$\therefore n = PV/RT$$

$$n = \frac{(1\text{atm.})(4.1\text{L})}{(0.082\text{L atm K}^{-1}\text{mol}^{-1})(300\text{K})} = \frac{1}{6} \text{ mol}$$

$$\text{now } n = \frac{\text{mass of gas}}{\text{Mol.mass of gas}} = \frac{1}{6} = \frac{7}{\text{mol.mass of gas}}$$

$$\begin{aligned}\text{Thus, molecular mass of gas} &= 7 \times 6 \\ &= 42 \text{ g mol}^{-1}\end{aligned}$$

Ex.18 Calculate density of ammonia at 30°C and 5 atm. pressure -

- (A) 3.03 g/litres. (B) 3.82 g/litres (C) 3.42 g/litres. (D) 4.42 g/litres.

Sol. (C)

$$PV = nRT, \quad \text{or} \quad PV = \frac{m}{M}RT \quad \text{or} \quad P = \frac{m}{V} \times \frac{RT}{M}$$

$$\text{or } P = d \times \frac{RT}{M}$$

$$d = MP/RT ; d = \frac{17 \times 5}{0.082 \times 303} = 3.42 \text{ g/litres.}$$

Ex.19 3 moles of a gas are present in a vessel at a temperature of 27°C . Calculate the value of gas constant (R) in terms of kinetic energy of the molecules of gas -

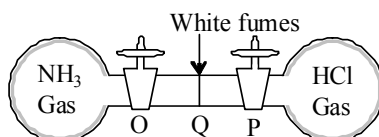
- (A) 7.4×10^{-4} KE per degree kelvin.
 (B) 4.5×10^{-4} KE per degree kelvin.
 (C) 7.4×10^{-5} KE per degree kelvin.
 (D) None of these

Sol. [A] K.E. for 1 mole = $\frac{3}{2}RT$

$$\text{K.E. for 3 moles} = \frac{9}{2}RT. \text{ or } R = \frac{2}{9T} \text{ KE} = \frac{2}{9(300)} \text{ KE}$$

$$= 7.4 \times 10^{-4} \text{ KE per degree kelvin.}$$

Ex.20 In the following diagram, container of NH_3 gas and container of HCl gas, connected through a long tube, are opened simultaneously at both ends; the white NH_4Cl ring first formed will be at Q point. If $OP = 40\text{cm}$, then find OQ -



- (A) 35 cm (B) 23.74 cm (C) 30 cm (D) 31.25 cm

Sol. [B]

$$\text{Let } OQ = x \text{ cm so } QP = (40 - x) \text{ cm}$$

Diffused volume of NH_3 gas = Area of T.S. of tube \times Distance travelled by NH_3 gas

$$V_{\text{NH}_3} = A \times \text{OQ} = Ax$$

{Where A is area of T.S. of tube}

Similarly in the same time,

Diffused volume of HCl gas = Area of T.S. of tube \times Distance travelled by HCl gas

$$V_{\text{HCl}} = A \times \text{QP} = A(40 - x)$$

From Graham's Law of diffusion

$$\Rightarrow \frac{r_{\text{NH}_3}}{r_{\text{HCl}}} = \sqrt{\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}}$$

$$\Rightarrow \frac{V_{\text{NH}_3/t}}{V_{\text{HCl}/t}} = \sqrt{\frac{36.5}{17}} = 1.46$$

$$\Rightarrow \frac{x}{(40 - x)} = 1.46$$

$$\Rightarrow x = 23.74 \text{ cm}$$

$$\therefore \text{OQ} = 23.74 \text{ cm}$$

Ex.21 The root mean square velocity of hydrogen is $\sqrt{5}$ times than that of nitrogen. If T is the temperature of the gas, then :

(A) $T_{\text{H}_2} = T_{\text{N}_2}$

(B) $T_{\text{H}_2} > T_{\text{N}_2}$

(C) $T_{\text{H}_2} < T_{\text{N}_2}$

(D) $T_{\text{H}_2} = \sqrt{7} T_{\text{N}_2}$

Sol. [C] $V_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \frac{(V_{\text{rms}})_{\text{H}_2}}{(V_{\text{rms}})_{\text{N}_2}} = \sqrt{\frac{T_{\text{H}_2}}{M_{\text{H}_2}} \times \frac{M_{\text{N}_2}}{T_{\text{N}_2}}}$;

$$(V_{\text{rms}})_{\text{H}_2} = \sqrt{5}(V_{\text{rms}})_{\text{N}_2}$$

$$\therefore \frac{(V_{\text{rms}})_{\text{H}_2}}{(V_{\text{rms}})_{\text{N}_2}} \times \sqrt{5} = \sqrt{\frac{T_{\text{H}_2}}{T_{\text{N}_2}} \times \frac{28}{2}}$$

$$= \frac{\sqrt{5}}{1} = \sqrt{\frac{T_{\text{H}_2}}{T_{\text{N}_2}} \times 14}$$

$$= 5 = \frac{T_{\text{H}_2}}{T_{\text{N}_2}} \times 14$$

$$T_{\text{N}_2} \times 5 = T_{\text{H}_2} \times 14$$

$$\therefore T_{\text{N}_2} > T_{\text{H}_2}$$

Ex.22 A jar contains a gas and a few drops of water. The pressure in the jar is 830 mm of Hg. The temperature of the jar is reduced by 1%. The vapour pressure of water at two temperature are 30 and 25 mm of Hg. Calculate the new pressure in jar.

- (A) 792 mm of Hg (B) 817 mm of Hg
(C) 800 mm of Hg (D) 840 mm of Hg

Sol. [B] $P_{\text{gas}} = P_{\text{dry gas}} + P_{\text{moisture}}$ at T K

$$\text{or } P_{\text{dry}} = 830 - 30 = 800$$

$$\text{Now at } T_2 = 0.99 T_1 ;$$

$$\text{at constant volume } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_{\text{dry}} = \frac{800 \times 0.99 T}{T} = 792 \text{ mm}$$

$$\therefore P_{\text{gas}} = P_{\text{dry}} + P_{\text{moisture}}$$

$$= 792 + 25 = 817 \text{ mm}$$

Ex.23 Calculate relative rate of effusion of O_2 to CH_4 through a container containing O_2 and CH_4 in 3 : 2 mass ratio.

- (A) $\frac{3\sqrt{2}}{4}$ (B) $\frac{3}{4\sqrt{2}}$ (C) $\frac{3}{2\sqrt{2}}$ (D) None of these

Sol. [B] $\frac{r_{\text{O}_2}}{r_{\text{CH}_4}} = \frac{n_{\text{O}_2}}{n_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{O}_2}}}$

$$= \frac{3}{2} \times \frac{16}{32} \times \sqrt{\frac{16}{32}} = \frac{3}{4\sqrt{2}}$$

Ex.24 At what temperature will average speed of the molecule of the second member of the series C_nH_{2n} be the same of Cl_2 at 627°C ?

- (A) 259.4 K (B) 400 K (C) 532.4 K (D) None of these

Sol. [C] Second member of C_nH_{2n} series $= \text{C}_3\text{H}_6 = 42$

$$= \sqrt{\frac{8RT_1}{\pi M_1}} = \sqrt{\frac{8RT_2}{\pi M_2}} = \frac{900}{71} = \frac{T_2}{42}$$

$$T_2 = 532.4 \text{ K}$$

Ex.25 80 mL of O_2 takes 2 minute to pass through the hole. What volume of SO_2 will pass through the hole in 3 minute ?

- (A) $\frac{120}{\sqrt{2}}$ (B) $120 \times \sqrt{2}$ (C) $\frac{12}{\sqrt{2}}$ (D) None of these

Sol. [A] $\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \frac{V_1 \times t_2}{V_2 \times t_1} = \sqrt{\frac{M_2}{M_1}};$

$$\frac{80 \times 3}{V_2 \times 2} = \sqrt{\frac{64}{32}} = \sqrt{2}; V_2 = \frac{120}{\sqrt{2}}$$

Ex.26 The density of a gas filled electric lamp is 0.75 kg/m^3 . After the lamp has been switched on, the pressure in it increases from $4 \times 10^4 \text{ Pa}$ to $9 \times 10^4 \text{ Pa}$. What is increase in U_{RMS} ?

- (A) 100 (B) 200 (C) 300 (D) None of these

Sol. [B] $U_1 = \sqrt{\frac{3P_1}{d_1}}$

$$\therefore \Delta U_{\text{rms}} = \sqrt{\frac{3}{d}} (\sqrt{P_2} - \sqrt{P_1})$$

$$= \sqrt{\frac{3}{0.75}} (300 - 200)$$

$$= \sqrt{4} \times 100 = 200$$

Ex.27 If one mole each of a monoatomic and diatomic gases are mixed at low temperature then C_p/C_v ratio for the mixture is :

- (A) 1.40 (B) 1.428 (C) 1.5 (D) 1.33

Sol. [C] $C_v = \frac{\left(\frac{3}{2}R + \frac{5}{2}R\right)}{2} = 2R$

$$C_p = \frac{\left(\frac{5}{2}R + \frac{7}{2}R\right)}{2} = 3R$$

$$\frac{C_p}{C_v} = 1.5$$

Ex.28 If one mole of a monoatomic gas ($\gamma = 5/3$) is mixed with one mole of a diatomic gas ($\gamma = 7/5$), the value of γ for the mixture is :

- (A) 1.4 (B) 1.5 (C) 1.53 (D) 3.07

Sol. [B]
$$\begin{cases} C_v = \frac{3}{2}RT \\ C_p = \frac{5}{2}RT \end{cases} \text{ for monoatomic gas;}$$

$$\begin{cases} C_v = \frac{5}{2}RT \\ C_p = \frac{7}{2}RT \end{cases} \text{ for diatomic gas;}$$

Thus, for mixture of 1 mole each,

$$C_v = \frac{\frac{3}{2}RT + \frac{5}{2}RT}{2} \text{ and } C_p = \frac{\frac{5}{2}RT + \frac{7}{2}RT}{2}$$

$$\text{Thus, } \frac{C_p}{C_v} = \frac{3RT}{2RT} = 1.5$$

Ex.29 The average speed at temperature $T^\circ\text{C}$ of $\text{CH}_4(\text{g})$ is $\sqrt{\frac{28}{88}} \times 10^3 \text{ ms}^{-1}$. What is the value of T ?

- (A) 240.55°C (B) -32.45°C (C) 3000°C (D) -24.055°C

Sol. [B] $\sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{28}{88}} = \sqrt{\frac{7}{22}}$

$$\frac{8 \times 8.314 \times T}{\pi \times 16 \times 10^{-3}} = \frac{7}{22} \times 10^6$$

$$T = \frac{1000 \times 2}{8.314} = 240.55 \text{ K}$$

$$T^\circ\text{C} = 240.55 - 273 = -32.45^\circ\text{C}$$

Ex.30 The intercept on y-axis and slope of curve plotted between P/T vs T

For an ideal gas having 10 moles in a closed rigid container of volume 821. L. (P = pressure in atm and T = Temp. in K, $\log_{10} 2 = 0.30$) are respectively

- (A) 0.01, 0 (B) 0.1, 1 (C) 0.1, 0 (D) 10, 1

Sol. [B] Intercept on y-axis

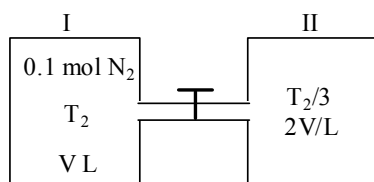
$$= \log_{10} \frac{nR}{V} = \log_{10} \frac{10 \times 0.0821}{8.21} = -1.0$$

$$\frac{P}{T} \text{ v/s curve } \frac{P}{T} = \frac{nR}{V}$$

$$\text{Intercept} = \frac{nR}{V} = \frac{10 \times 0.0821}{8.21} = 0.1, \text{ slope} = 0$$

Ex.31 Two vessels connected by a valve of negligible volume. One container (I) has 2.8 g of N_2 at temperature T_1 (K). The other container (II) is completely evacuated. The container (I) is heated to T_2 (K) while container (II) is maintained at $T_2/3$ (K). volume of vessel (I) is half that of vessel (II). If the valve is opened then what is the weight ratio of N_2 in both vessel (W_I/W_{II}) ?

- (A) 1 : 2 (B) 1 : 3 (C) 1 : 6 (D) 3 : 1

Sol. [C]

Let x mole of N_2 present into vessel II and P is final pressure of N_2

$$P(2V) = xR(T_2/3) \text{ and } P(V) = (0.1 - x)RT_2$$

$$\Rightarrow 2 = \frac{x}{3(0.1 - x)}$$

$$\Rightarrow x = 0.6/7 \text{ mole}$$

$$\frac{0.6}{7} \times 28 \Rightarrow 2.4 \text{ g } N_2$$

II has 2.4 g N_2 and I has 0.4 g of N_2 ;

$$\frac{W_I}{W_{II}} = \frac{0.4}{2.4} \Rightarrow 1 : 6$$

Ex.32 Two closed vessel A and B of equal volume containing air at pressure P_1 and temperature T_1 are connected to each other through a narrow open tube. If the temperature of one is now maintained at T_1 and other at T_2 (where $T_1 > T_2$) then that what be the final pressure ?

(A) $\frac{T_1}{2P_1T_2}$

(B) $\frac{2P_1T_2}{T_1 + T_2}$

(C) $\frac{2P_1T_1}{T_1 - T_2}$

(D) $\frac{2P_1}{T_1 + T_2}$

Sol. [D] Let $T_1 > T_2$; final pressure will be same, Let x mole transfer from A to B vessel.

$$\therefore P_A V = (n - x)RT$$

$$\text{and } P_A V = (n + x)RT_2$$

$$\therefore x = \frac{n(T_1 - T_2)}{T_1 + T_2}$$

$$\text{finally } P_1 \times 2V = 2nRT_1; V = \frac{nRT_1}{P_1}$$

$$\therefore P_A \times \frac{nRT_1}{P_1} = \left(n - \frac{n(T_1 - T_2)}{(T_1 + T_2)} \right) RT_1$$

$$P_A = \frac{2P_1T_2}{T_1 + T_2}$$

Ex.33 7 moles of a tetra-atomic non-linear gas 'A' at 10 atm and T K are mixed with 6 moles of another gas B at $\frac{T}{3}$ K and 5 atm in a closed, rigid vessel without energy transfer with surroundings. If final temperature of mixture was $\frac{5T}{6}$ K, then gas B is ? (Assuming all modes of energy are active)

- (A) monatomic (B) diatomic (C) triatomic (D) tetra atomic

Sol. [B] C_v of gas A = $\frac{3}{2}R + \frac{3}{2}R + 6R = 9R$

Let C_v of gas B = X

$$\text{Heat lost by gas A} = 7 \times 9R \times \left(T - \frac{5T}{6}\right)$$

$$\text{Heat gained by gas B} = 6X \left(\frac{5T}{6} - \frac{T}{3}\right)$$

$$\Rightarrow 63R \left(\frac{T}{6}\right) = 6X \left(\frac{T}{2}\right) = X = \frac{7}{2} R;$$

\therefore gas is dia atomic

Ex.34 A balloon of diameter 2 meter weight 100 kg. Calculate its pay-load, if it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kg m^{-3} . (Given : $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

- (A) 4952.42 kg (B) 4932.42 kg
(C) 493.242 kg (D) None of these

Sol. [B] Weight of balloon = 100 kg = 10×10^4 g volume of balloon = $\frac{4}{3} \pi r^3$

$$= \frac{4}{3} \times \frac{22}{7} \times \left(\frac{21}{2}\right)^3$$

$$= 4851 \text{ m}^3 = 4851 \times 10^3 \text{ L}$$

$$\text{Weight of gas (He) in balloon} = \frac{PVM}{RT}$$

$$= \frac{1 \times 4851 \times 10^3 \times 4}{0.082 \times 300}$$

$$= 78.878 \times 10^4$$

\therefore Total weight of gas and balloon

$$= 78.878 \times 10^4 + 10 \times 10^4$$

$$= 88.878 \times 10^4 \text{ g or } 888.78 \text{ kg}$$

$$\text{Weight of air displaced} = 1.2 \times 4851 = 5821.2 \text{ kg}$$

\therefore Pay load = wt. of air displaced – wt. of

(balloon + gas)

$$\therefore \text{Pay load} = 5821.2 - 888.78 = 4932.42 \text{ kg}$$

Ex.35 The density of vapour of a substance (X) at 1 atm pressure and 500 K is 0.8 kg/m³. The vapour effuses through a small hole at a rate of 4/5 times slower than oxygen under the same condition. What is the compressibility factor (Z) of the vapour ?

- (A) 0.974 (B) 1.35
(C) 1.52 (D) 1.22

Sol. [C] $\frac{r_x}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_x}} = \left(\frac{4}{5}\right)^2 = \frac{32}{M_x} = M_x = 50$

$d_x = 0.80 \text{ kg/m}^3,$

$V_m = \frac{1000}{800} \times 50 = 62.5 \text{ L}$

$Z = \frac{PV_m}{RT} = \frac{1 \times 62.5}{0.0821 \times 500} = 1.52$

Ex.36 A given volume of ozonised oxygen (containing 60% oxygen by volume) required 220 sec to effuse which an equal volume of oxygen took 200 sec only under the conditions. If density of O₂ is 1.6 g/L then find density of O₃.

- (A) 1.936 g/L (B) 2.16 g/L
(C) 3.28 g/L (D) 2.24 g/L

Sol. [D] Let V mL of gas effused

$\frac{V/220}{V/200} = \sqrt{\frac{d_{O_2}}{d_{\text{mix}}}} \Rightarrow d_{\text{mix}} = 1.6 \times (1.1)^2 = 1.936 \text{ g/L}$

Let density of ozone is d; In 100 volume ozonised oxygen, 60% O₂ and 40% by volume O₃ is present

∴ Mass of mixture = mass of ozone + mass of oxygen

$100 \times 1.936 = 40 \times d + 60 \times 1.6$

density of O₃ is 2.44 g/L

Ex.37 For a real gas (mol. mass = 60) if density at critical point is 0.80 g/cm³ and its

$T_c = \frac{4 \times 10^5}{821} \text{ K}$, then van der Waals' constant a (in atm L² mol⁻²) is

- (A) 0.3375 (B) 3.375
(C) 1.68 (D) 0.025

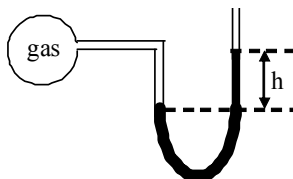
Sol. [B] $V_c = \frac{60}{0.80} = 75 \text{ cm}^3 \text{ mol}^{-1};$

$$b = \frac{V_c}{3} = 25 \text{ cm}^3 \text{ mol}^{-1} = 0.025 \text{ L mol}^{-1}$$

$$T_c = \frac{8a}{27Rb}$$

$$\frac{4 \times 10^5}{821} = \frac{8 \times a}{27 \times 0.0821 \times 0.025} \Rightarrow a = 3.375$$

Ex.38 A bulb of constant volume is attached to a manometer tube open at other end as shown in figure. The manometer is filled with a liquid of density $(1/3)^{\text{rd}}$ that of mercury. Initially h was 228 cm.



Through a small hole in the bulb gas leaked assuming pressure decreases as $\frac{dp}{dt} = -kP$. If value of h is 114 cm after 14 minutes. What is the value of k (in hour^{-1}) ?

[Use : $\ln(4/3) = 0.28$ and density of Hg = 13.6 g/mL.]

- (A) 0.6 (B) 1.2
(C) 2.4 (D) None of these

Sol. [B] $P = P_0 e^{-kt}$; $P_0 = \frac{228}{3} + 76 = 152 \text{ cm Hg}$

At $t = 14 \text{ min}$; $P = \frac{114}{3} + 76 = 114 \text{ cm Hg}$

$$\therefore 152e^{-kt} = 114$$

$$\Rightarrow k = \frac{1}{t} \ln \frac{152}{114} = \frac{1}{14} \times 0.28$$

$$= 0.02 \times 60 \text{ hr}^{-1} = 1.2 \text{ hr}^{-1}$$

Ex.39 A balloon weighing 50 kg is filled with 685 kg of helium at 1 atm pressure and 25°C. What will be its pay load if it displaced 5108 kg of air ?

- (A) 4373 kg (B) 4423 kg
(C) 5793 kg (D) None of these

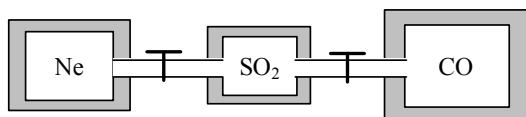
Sol. [A] Mass of the filled balloon = 50 + 685 = 735 kg

Pay load = Mass of displaced air

– Mass of balloon

$$= 5108 - 735 = 4373 \text{ kg}$$

Ex.40 Three closed rigid vessels, A,B and C without energy transfer with surroundings, which initially contain three different gases at different temperature are connected by tube of negligible volume. The vessel A contain 2 mole Ne gas, at 300 K, vessel 'B' contain 2 mole SO_2 gas at 400 K and vessel 'C' contain 3 mole CO gas at 500 K. What is the final pressure (in atm) attained by gases when all valves of connecting three vessels are opened and additional 15.6 kcal heat supplied to vessel through valve. The volume of A,B and C vessel is 2,2 and 3 litre respectively.



Given : $R = 2 \text{ calorie/mol-K}$; $C_v(\text{Ne}) = \frac{3}{2} R$, $C_v(\text{CO}) = \frac{5}{2} R$ and $C_v(\text{SO}_2) = 3 R$

- (A) 73.89 atm (B) 67.31 atm
(C) 80 atm (D) None of these

Sol. [A] Total heat received by gas = heat provided

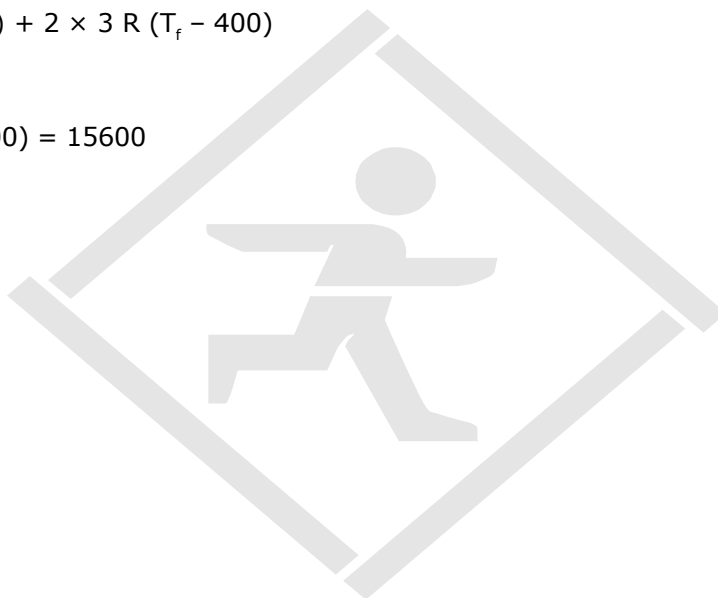
$$2 \times \frac{3}{2} R (T_f - 300) + 2 \times 3 R (T_f - 400)$$

$$+ 3 \times \frac{5}{2} R (T_f - 500) = 15600$$

$$T_f = 900 \text{ K}$$

$$P_f = \frac{900 \times 0.0821 \times 7}{7}$$

$$P_f = 73.89 \text{ atm}$$



EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)**

1. At constant temperature, in a given mass of an ideal gas -
 (A) The ratio of pressure and volume always remains constant
 (B) Volume always remains constant
 (C) Pressure always remains constant
 (D) The product of pressure and volume always remains constant

Sol.

2. Three flasks of equal volumes contain CH_4 , CO_2 and Cl_2 gases respectively. They will contain equal number of molecules if -
 (A) the mass of all the gases is same
 (B) the moles of all the gas is same but temperature is different
 (C) pressure of all the flasks are same
 (D) temperature, pressure are same in the flasks

Sol.

3. A certain mass of a gas occupies a volume of 2 litres at STP. Keeping the pressure constant at what temperature would the gas occupy a volume of 4 litres -
 (A) 546°C (B) 273°C
 (C) 100°C (D) 50°C

Sol.

4. If 500 ml of a gas 'A' at 1000 torr and 1000 ml of gas B at 800 torr are placed in a 2L container, the final pressure will be-
 (A) 100 torr (B) 650 torr
 (C) 1800 torr (D) 2400 torr

Sol.

5. Two flasks A and B of 500 ml each are respectively filled with O_2 and SO_2 at 300 K and 1 atm. pressure. The flasks will contain-
 (A) The same number of atoms
 (B) The same number of molecules
 (C) More number of moles in flask A as compared to flask B
 (D) The same amount of gases

Sol.

6. In the gas equation $PV = nRT$, the value of universal gas constant would depend only on -
 (A) The nature of the gas
 (B) The pressure of the gas
 (C) The temperature of the gas
 (D) The units of measurement

Sol.

7. A 0.5 dm^3 flask contains gas 'A' and 1 dm^3 flask contains gas 'B' at the same temperature. If density of A = 3.0 gm dm^{-3} and that of B = 1.5 gm dm^{-3} and the molar mass of A = $1/2$ of B, then the ratio of pressure exerted by gases is-
 (A) $P_A/P_B = 2$ (B) $P_A/P_B = 1$
 (C) $P_A/P_B = 4$ (D) $P_A/P_B = 3$.

Sol.

8. When the pressure of 5L of N_2 is doubled and its temperature is raised from 300K to 600K, the final volume of the gas would be-
 (A) 10 L (B) 5 L
 (C) 15 L (D) 20 L

Sol.

9. If the pressure of a gas contained in a closed vessel is increased by 0.4% when heated by 1°C its initial temperature must be :
 (A) 250 K (B) 250°C
 (C) 25°C (D) 25 K

Sol.

10. A thin balloon filled with air at 47°C has a volume of 3 litre. If on placing it in a cooled room its volume becomes 2.7 litre, the temperature of room is :
 (A) 42° (B) 100°C
 (C) 15°C (D) 200°C

Sol.

11. If a mixture containing 3 moles of hydrogen and 1 mole of nitrogen is converted completely into ammonia, the ratio of initial and final volume under the same temperature and pressure would be:
 (A) 3 : 1 (B) 1 : 3
 (C) 2 : 1 (D) 1 : 2

Sol.

12. SO_2 at STP contained in a flask was replaced by O_2 under identical conditions of pressure, temperature and volume. Then the weight of O_2 will be _____ SO_2 .
 (A) half (B) one fourth
 (C) twice (D) four times

Sol.

13. Assuming that O_2 molecule is spherical in shape with radius 2\AA , the percentage of the volume of O_2 molecules to the total volume of gas at S.T.P. is :
 (A) 0.09% (B) 0.9%
 (C) 0.009% (D) 0.045%

Sol.

14. Two flasks of equal volume are connected by a narrow tube (of negligible volume) all at 27°C and contain 0.70 mole of H_2 at 0.5 atm. One of the flask is then immersed into a bath kept at 127°C , while the other remains at 27°C . The final pressure in each flask is :
 (A) Final pressure = 0.5714 atm
 (B) Final pressure = 1.5714 atm
 (C) Final pressure = 0.5824 atm
 (D) None of these

Sol.

15. Two flasks of equal volume are connected by a narrow tube (of negligible volume) all at 27°C and contain 0.70 moles of H_2 at 0.5 atm. One of the flask is then immersed into a bath kept at 127°C , while the other remains at 27°C . The number of moles of H_2 in flask 1 and flask 2 are :
 (A) Moles in flask 1 = 0.4, Moles in flask 2 = 0.3
 (B) Moles in flask 1 = 0.2, Moles in flask 2 = 0.3
 (C) Moles in flask 1 = 0.3, Moles in flask 2 = 0.2
 (D) Moles in flask 1 = 0.3, Moles in flask 2 = 0.2

Sol.

16. A gas is heated from 0°C to 100°C at 0.1 atm pressure. If the initial volume of the gas is 10.0 l, its final volume would be :
 (A) 7.32 l (B) 10.00 l
 (C) 13.66 l (D) 20.00 l

Sol.

17. Under what conditions will a pure sample of an ideal gas not only exhibit a pressure of 1 atm but also a concentration of 1 mol litre^{-1} . [$R = 0.0892 \text{ litre atm mol}^{-1} \text{ K}^{-1}$]
 (A) at S.T.P.
 (B) when $V = 22.42 \text{ L}$
 (C) when $T = 12 \text{ K}$
 (D) impossible under any condition

Sol.

18. A and B are two identical vessels. A contains 15 g ethane at 1 atm and 298 K. The vessel B contains 75 g of a gas X_2 at same temperature and pressure. The vapour density of X_2 is :

(A) 75 (B) 150
(C) 37.5 (D) 45

Sol.

19. The density of neon will be highest at :
(A) STP (B) 0°C , 2 atm
(C) 273°C , 1 atm (D) 273°C , 2 atm

Sol.

20. A 0.5 dm^3 flask contains gas A and 1 dm^3 flask contains gas B at the same temperature. If density of A = 3 g/dm^3 and that of B = 1.5 g/dm^3 and the molar mass of A = $1/2$ of B, the ratio of pressure exerted by gases is :

(A) $\frac{P_A}{P_B} = 2$ (B) $\frac{P_A}{P_B} = 1$
(C) $\frac{P_A}{P_B} = 4$ (D) $\frac{P_A}{P_B} = 3$

Sol.

DALTONS LAW OF PARTIAL PRESSURE

21. A cylinder is filled with a gaseous mixture containing equal masses of CO and N_2 . The partial pressure ratio is :

(A) $P_{N_2} = P_{CO}$ (B) $P_{CO} = 0.875 P_{N_2}$
(C) $P_{CO} = 2 P_{N_2}$ (D) $P_{CO} = \frac{1}{2} P_{N_2}$

Sol.

22. A gas X diffuses three times faster than another gas Y the ratio of their densities i.e., $D_X : D_Y$ is-

(A) $\frac{1}{3}$ (B) $\frac{1}{9}$ (C) $\frac{1}{6}$ (D) $\frac{1}{12}$

Sol.

23. At STP, a container has 1 mole of Ar, 2 moles of CO_2 , 3 moles of O_2 and 4 moles of N_2 . Without changing the total pressure if one mole of O_2 is removed, the partial pressure of O_2 :

(A) is changed by about 26 %
(B) is halved
(C) is unchanged
(D) changed by 33 %

Sol.

24. Equal weights of ethane & hydrogen are mixed in an empty container at 25°C , the fraction of the total pressure exerted by hydrogen is :

(A) 1 : 2 (B) 1 : 1
(C) 1 : 16 (D) 15 : 16

Sol.

25. A mixture of hydrogen and oxygen at one bar pressure contains 20% by weight of hydrogen. Partial pressure of hydrogen will be :

(A) 0.2 bar (B) 0.4 bar
(C) 0.6 bar (D) 0.8 bar

Sol.

26. A compound exists in the gaseous phase both as monomer (A) and dimer (A_2). The atomic mass of A is 48 and molecular mass of A_2 is 96. In an experiment 96 g of the compound was confined in a vessel of volume 33.6 litre and heated to 237°C . The pressure developed if the compound exists as dimer to the extent of 50% by weight under these conditions will be :

(A) 1 atm (B) 2 atm
(C) 1.5 atm (D) 4 atm

Sol.

GRAHAMS LAW OF DIFFUSION

27. Three footballs are respectively filled with nitrogen, hydrogen and helium. If the leaking of the gas occurs with time from the filling hole, then the ratio of the rate of leaking of gases ($r_{N_2} : r_{H_2} : r_{He}$) from three footballs (in equal time interval) is :

- (A) $(1 : \sqrt{14} : \sqrt{7})$ (B) $(\sqrt{14} : \sqrt{7} : 1)$
 (C) $(\sqrt{7} : 1 : \sqrt{14})$ (D) $(1 : \sqrt{7} : \sqrt{14})$

Sol.

28. The rates of diffusion of SO_3 , CO_2 , PCl_3 and SO_2 are in the following order-

- (A) $PCl_3 > SO_3 > SO_2 > CO_2$
 (B) $CO_2 > SO_2 > PCl_3 > SO_3$
 (C) $SO_2 > SO_3 > PCl_3 > CO_2$
 (D) $CO_2 > SO_2 > SO_3 > PCl_3$

Sol.

29. 20 l of SO_2 , diffuses through a porous partition in 60 seconds. Volume of O_2 diffuse under similar conditions in 30 seconds will be :

- (A) 12.14 l (B) 14.14 l
 (C) 18.14 l (D) 28.14 l

Sol.

30. See the figure :



The valves of X and Y opened simultaneously. The white fumes of NH_4Cl will first form at :

- (A) A (B) B
 (C) C (D) A, B and C simultaneously

Sol.

31. X ml of H_2 gas of effuses through a hole in a container in 5 sec. The time taken for the effusion of the same volume of the gas specified below under identical conditions is :

- (A) 10 sec. He (B) 20 sec. O_2
 (C) 25 sec. CO_2 (D) 55 sec. CO_2

Sol.

KINETIC THEORY OF GASES

32. At what temperature will the total KE of 0.3 mol of He be the same as the total KE of 0.40 mol of Ar at 400 K ?

- (A) 533 K (B) 400 K
 (C) 346 K (D) 300 K

Sol.

33. By how many folds the temp of a gas would increase when the r.m.s. velocity of gas molecules in a closed container of fixed volume is increased from $5 \times 10^4 \text{ cm s}^{-1}$ to $10 \times 10^4 \text{ cm s}^{-1}$ -

- (A) 0.5 times (B) 2 times
 (C) 4 times (D) 16 times.

Sol.

34. The root mean square velocity of an ideal gas in a closed container of fixed volume is increased from $5 \times 10^4 \text{ cm. s}^{-1}$ to $10 \times 10^4 \text{ cm. s}^{-1}$. Which of the following statements might correctly explain how the change accomplished -

- (A) By heating the gas, the temperature is doubled
 (B) By heating the gas, the pressure is made four times

(C) By heating the gas, the volume is tripled

(D) By heating the gas, the pressure is doubled.

Sol.

- 35.** The temperature of an ideal gas is increased from 140 K to 560 K. If at 140 K the root-mean square velocity of the gas molecules is V , at 560 K it becomes :

(A) $5V$ (B) $2V$
(C) $V/2$ (D) $V/4$

Sol.

- 36.** Which of the following gas molecules has the longest mean-free path ?

(A) H_2 (B) N_2
(C) O_2 (D) Cl_2

Sol.

- 37.** Temperature at which r.m.s. speed of O_2 is equal to that of neon at 300 K is :

(A) 280 K (B) 480 K
(C) 680 K (D) 180 K

Sol.

- 38.** The R.M.S speed of the molecules of a gas of density 4 kg m^{-3} and pressure $1.2 \times 10^5 \text{ N m}^{-2}$ is:

(A) 120 ms^{-1} (B) 300 ms^{-1}
(C) 600 ms^{-1} (D) 900 ms^{-1}

Sol.

- 39.** The mass of molecule A is twice that of molecule B. The root mean square velocity of molecule A is twice that of molecule B. If two containers of equal volume have same number of molecules, the ratio of pressure P_A/P_B will be:

(A) 8 : 1 (B) 1 : 8
(C) 4 : 1 (D) 1 : 4

Sol.

- 40.** The temperature of an ideal gas is increased from 120 K to 480 K. If at 120 K the root-mean-square velocity of the gas molecules is v , at 480 K it becomes -

(A) $4v$ (B) $2v$
(C) $v/2$ (D) $v/4$

Sol.

- 41.** The ratio between the r.m.s velocity of H_2 of 50 K and that of O_2 at 800 K is :

(A) 4 (B) 2
(C) 1 (D) $1/4$

Sol.

REAL GASES

- 42.** The Van der Waal's parameters for gases W, X, Y and Z are -

Gas	$a(\text{atm L}^2 \text{ mol}^{-2})$	$b(\text{Lmol}^{-1})$
W	4.0	0.027
X	8.0	0.030
Y	6.0	0.032
Z	12.0	0.027

Which one of these gases has the highest critical temperature ?

(A) W (B) X
(C) Y (D) Z

Sol.

43. The correct relationship between T_C , T_B and T_i is -
 (A) $T_C < T_B < T_i$ (B) $T_C > T_B > T_i$
 (C) $T_C < T_i < T_B$ (D) $T_i < T_B < T_C$

Sol.

44. A real gas obeying Vander Waal equation will resemble ideal gas, if the :
 (A) constants a & b are small
 (B) a is large & b is small
 (C) a is small & b is large
 (D) constant a & b are large

Sol.

45. For the non-zero values of force of attraction between gas molecules, gas equation will be :

- (A) $PV = nRT - \frac{n^2a}{V}$
 (B) $PV = nRT + nbP$
 (C) $PV = nRT$
 (D) $P = \frac{nRT}{V - b}$

Sol.

46. Compressibility factor for H_2 behaving as real gas is :

- (A) 1 (B) $\left(1 - \frac{a}{RTV}\right)$
 (C) $\left(1 + \frac{Pb}{RT}\right)$ (D) $\frac{RTV}{(1 - a)}$

Sol.

47. At low pressure, the van der Waal's equation is written as $\left[p + \frac{a}{V^2}\right] V = RT$.

The compressibility factor is then equal to :

- (A) $\left(1 - \frac{a}{RTV}\right)$ (B) $\left(1 - \frac{RTV}{a}\right)$
 (C) $\left(1 + \frac{a}{RTV}\right)$ (D) $\left(1 + \frac{RTV}{a}\right)$

Sol.

48. In vander Waals equation of state for a non ideal gas the term that accounts for intermolecular forces is :

- (A) nb (B) nRT
 (C) n^2a/V^2 (D) $(nRT)^{-1}$

Sol.

49. The values of Vander Waals constant " a " for the gases O_2 , N_2 , NH_3 , & CH_4 , are 1.36, 1.39, 4.17, 2.253 $L^2 \text{ atm mole}^{-2}$ respectively. The gas which can most easily be liquified is:

- (A) O_2 (B) N_2
 (C) NH_3 (D) CH_4

Sol.

50. The correct order of normal boiling points of O_2 , N_2 , NH_3 , and CH_4 , for whom the values of vander Waals constant ' a ' are 1.360, 1.390, 4.170 and 2.253 $L^2 \text{ atm mol}^{-2}$ respectively, is

- (A) $O_2 < N_2 < NH_3 < CH_4$
 (B) $O_2 < N_2 < CH_4 < NH_3$
 (C) $NH_3 < CH_4 < N_2 < O_2$
 (D) $NH_3 < CH_4 < O_2 < N_2$

Sol.

Exercise - II**MULTIPLE CHOICE PROBLEMS(JEE ADVANCED)**

1. The ratio between the r. m. s. velocity of H_2 at 50 K and that of O_2 at 800 K is :
 (A) 4 (B) 2
 (C) 1 (D) $1/4$

Sol.

2. X ml of H_2 gas effuses through a hole in a container in 5 sec. The time taken for the effusion of the same volume of the gas specified below under identical conditions is :
 (A) 10 sec, He (B) 20 sec, O_2
 (C) 25 sec, CO (D) 55 sec, CO_2

Sol.

3. One mole of N_2O_4 (g) at 300 K is kept in a closed container under one atm. It is heated to 600 K when 20 % by mass of N_2O_4 (g) decomposes to NO_2 (g). The resultant pressure is :
 (A) 1.2 atm (B) 2.4 atm
 (C) 2.0 atm (D) 1.0 atm

Sol.

4. The absolute temperature of an ideal gas is _____ to/than the average kinetic energy of the gas molecules.

Sol.

5. One way of writing the equation of state for real gases is,

$$P \bar{V} = RT \left[1 + \frac{B}{\bar{V}} + \dots \right]$$

where B is a constant.

Derive an approximate expression for 'B' in terms of Vander Waals constant 'a' & 'b'.

Sol.

6. Calculate the total pressure in a 10 litre cylinder which contains 0.4 g He, 1.6 g oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of He gas in the cylinder. Assume ideal behaviour for gases.

Sol.

7. According to Graham's law, at a given temperature the ratio of the rates of diffusion $\frac{r_A}{r_B}$ of gases A and B is given by :

$$\begin{aligned} \text{(A)} \quad \frac{P_A}{P_B} \left(\frac{M_A}{M_B} \right)^{1/2} & \quad \text{(B)} \quad \left(\frac{M_A}{M_B} \right) \left(\frac{P_A}{P_B} \right)^{1/2} \\ \text{(C)} \quad \frac{P_A}{P_B} \left(\frac{M_B}{M_A} \right)^{1/2} & \quad \text{(D)} \quad \frac{M_A}{M_B} \left(\frac{P_B}{P_A} \right)^{1/2} \end{aligned}$$

Sol.

8. An evacuated glass vessel weighs 50.0 g when empty, 148.0 gm when filled with a liquid of density 0.98 g /mL and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas.

Sol.

9. Using Vander Waals equation, calculate the constant "a" when 2 moles of a gas confined in a 4 litre flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of "b" is 0.05 litre mol⁻¹.

Sol.

10. The pressure exerted by 12 g of an ideal gas at temperature t °C in a vessel of volume V is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10 %. Calculate the temperature 't' and volume 'V'. [molecular weight of gas = 120]

Sol.

11. One mole of N₂ gas at 0.8 atm takes 38 sec to diffuse through a pin hole, whereas one mole of an unknown compound of Xenon with F at 1.6 atm takes 57 sec to diffuse through the same hole. Calculate the molecular formula of the compound. (At. wt. Xe = 138, F = 19)

Sol.

12. A gas will approach ideal behaviour at :
(A) low temperature and low pressure
(B) low temperature and high pressure
(C) low pressure and high temperature
(D) high temperature and high pressure.

Sol.

13. The compressibility of a gas is less than unity at STP. Therefore
(A) $V_m > 22.4 \text{ L}$ (B) $V_m < 22.4 \text{ L}$
(C) $V_m = 22.4 \text{ L}$ (D) $V_m = 44.8 \text{ L}$

Sol.

14. The r. m. s. velocity of hydrogen is $\sqrt{7}$ times the r. m. s. velocity of nitrogen. If T is the temperature of the gas :
(A) $T(\text{H}_2) = T(\text{N}_2)$ (B) $T(\text{H}_2) > T(\text{N}_2)$
(C) $T(\text{H}_2) < T(\text{N}_2)$ (D) $T(\text{H}_2) = \sqrt{7} T(\text{N}_2)$

Sol.

15. The pressure of a fixed amount of an ideal gas is proportional to its temperature. Frequency of collision and their impact both increase in proportion to the square root of temperature. True/False.

Sol.

16. The root mean square velocity of an ideal gas at constant pressure varies with density as
 (A) d^2 (B) d
 (C) $d^{1/2}$ (D) $1/d^{1/2}$

Sol.

17. The compression factor (compressibility factor) for one mole of a vander Waals gas at 0°C and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the vander Waals constant 'a'.

Sol.

More than one correct:

18. Select the correct observation for a 8.21 lit container, filled with 2 moles of He at 300 K.,
 (A) It has pressure 6 atm
 (B) If it is an open rigid container, its pressure increases to 8 atm on heating to 400 K.
 (C) If it is closed non-rigid (like thin skin balloon), its volume increases to 16.42 lit. on heating to 600 K
 (D) When connected with another similar empty container maintained at 150 K while maintaining original container at 300 K, pressure reduces to $\frac{2}{3}$ atm.

Sol.

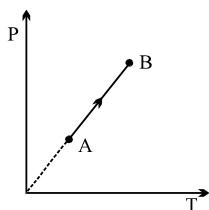
19. For 2 mol of CO_2 gas at 300 K
 (A) Translational kinetic energy is 1800 cal
 (B) Ratio of rotational to vibrational kinetic energy is (all degrees of freedom are activated) 1 : 2
 (C) Ratio of U_{rms} to U_{mps} is 3 : 2
 (D) Slope of $(\log P)$ vs $(\log V)$ curve is $\log(600 R)$.

Sol.

20. Select the incorrect statement(s):
 (A) At Boyle's temperature a real gas behaves like an ideal gas irrespective of pressure.
 (B) At critical condition, a real gas behaves like an ideal gas.
 (C) On increasing the temperature four times, collision frequency (Z_{11}) becomes double at constant volume.
 (D) At high pressure Vander Waal's constant 'b' dominates over 'a'.

Sol.

21. Select the correct option for an ideal gas undergoing a process as shown in diagram.



- (A) If 'n' is changing, 'V' must also be changing.
 (B) If 'n' is constant, 'V' must be constant.
 (C) If 'n' is constant, 'V' must be changing.
 (D) If 'n' is changing, 'V' must be constant.

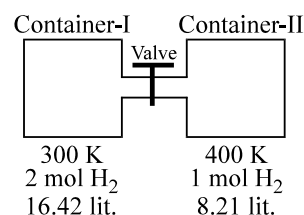
Sol.

22. Select the correct option(s) for an ideal gas

- (A) Most probable speed increases with increase in temperature
 (B) Fraction of particles moving with most probable speed increases with increase in temperature
 (C) Fraction of particles moving with most probable speed are more for Cl_2 than H_2 under similar condition of T, P & V.
 (D) Most probable speed is more for Cl_2 than H_2 at same temperature

Sol.

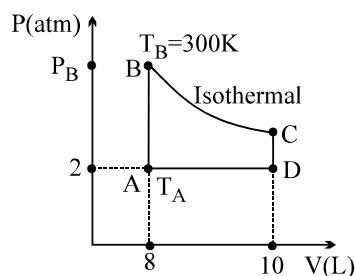
23. Select the correct option(s):



- (A) Pressure in container-I is 3 atm before opening the valve.
 (B) Pressure after opening the valve is 3.57 atm.
 (C) Moles in each compartment are same after opening the valve.
 (D) Pressure in each compartment are same after opening the valve.

Sol.

24. An ideal gas having 2 moles (fixed) is subjected to the changes as shown in (P-V) diagram. Select the correct option(s) from the following diagram.



(A) Temperature at "A" $\left(\frac{16}{R}\right)$; Pressure at "C" (60 R)

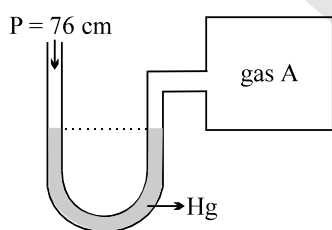
(B) Temperature at "D" $\left(\frac{10}{R}\right)$; Pressure at "B" (75 R)

(C) Temperature at "A" $\left(\frac{8}{R}\right)$; Pressure at "B" (75 R)

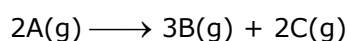
(D) Temperature at "D" $\left(\frac{5}{R}\right)$; Pressure at "C" (60 R)

Sol.

- 25.** An open ended mercury manometer is used to measure the pressure exerted by a trapped gas as shown in the figure. Initially manometer shows no difference in mercury level in both columns as shown in diagram.



After sparking 'A' dissociates according to following reaction



If pressure of Gas "A" decreases to 0.8 atm. Then (Assume temperature to be constant and is 300 K)

- (A) total pressure increased by 1.3 atm
 (B) total pressure increased by 0.3 atm
 (C) total pressure increased by 22.3 cm of Hg
 (D) difference in mercury level is 228 mm.

Sol.

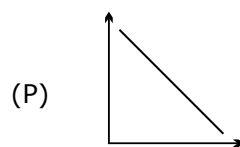
Match the column:

- 26.** Match the entries in **column I** with entries in **Column II** and then pick out correct options.

Column I

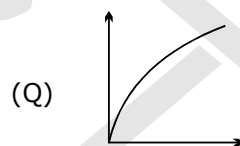
Column II

- (A) $\frac{1}{V^2}$ vs P for ideal gas at



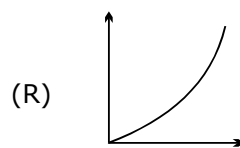
constant T and n.

- (B) V vs $\frac{1}{T}$ for ideal gas at



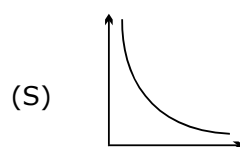
constant P and n

- (C) log P vs log V for ideal gas



at constant T and n.

- (D) V vs $\frac{1}{P^2}$ for ideal gas



at constant T and n.

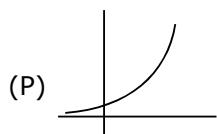
Sol.

27. Match the description in **Column I** with graph provided in **Column II**. For n moles of ideal gas at emperature 'T'.

Column I

Column II

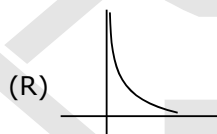
(A) $\frac{P}{V}$ vs P



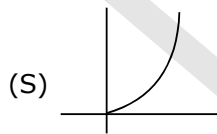
(B) $\frac{P}{V}$ vs V



(C) $\frac{V}{P}$ vs P^{-2}



(D) $\frac{P}{V}$ vs $\log P$



Sol.

Comprehension

Question No. 29 to 31 are based on the following Passage. Read it carefully & answer the questions that follow

Two containers X & Y are present with container X consisting of some mass of He at some temperature while container Y having double the volume as that of container X & kept at same temperature containing same mass of H_2 gas as the mass of Helium gas. Based on this data & the following conditions answer the question that follows

Assume sizes of H_2 molecule & He atom to be same & size of H-atom to be half to that of He-atom & only bimolecular collisions to be occurring.

Condition I: all except one atom of He are stationary in cont. X & all molecules of H_2 are moving in container Y.

Condition II: both containers contain all moving molecules

28. Assuming **condition I** to be applicable & if no. of *total collisions* occurring per unit time is 'A' in container X then no. of total collisions made by any one molecule in container Y will be:

- (A) A (B) $\sqrt{2} A$
(C) $\frac{A}{\sqrt{2}}$ (D) none of these

Sol.

29. Assuming **condition II** then ratio of 'total no. of collisions per unit volume per unit time' in container X & container Y is (container X : container Y)

(A) 1:1 (B) $\sqrt{2}:1$
(C) $1:\sqrt{2}$ (D) 4:1

Sol.

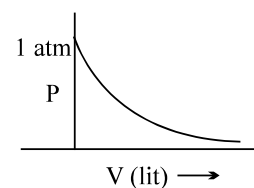
30. Assuming **condition II** to be applicable, if temperature only of container Y is doubled to that of original (causing dissociation of all H_2 gas into H gaseous atoms) then, if no. of total collisions per unit volume per unit time in container X is A then, no. of 'total collisions made by all molecules per unit volume in container Y would be

(A) $2\sqrt{2} A$ (B) $\sqrt{2} A$
(C) $8\sqrt{2} A$ (D) none of these

Sol.

Question No. 32 to 35 are based on the following Passage. Read it carefully & answer the questions that follow

On the recently discovered 10th planet it has been found that the gases follow the relationship $P e^{V/2} = nCT$ where C is constant other notation are as usual (V in lit., P in atm and T in Kelvin). A curve is plotted between P and V at 500 K & 2 moles of gas as shown in figure



31. The value of constant C is
(A) 0.01 (B) 0.001
(C) 0.005 (D) 0.002

Sol.

32. Find the slope of the curve plotted between P Vs T for closed container of volume 2 lit. having same moles of gas

(A) $\frac{e}{2000}$ (B) $2000 e$
(C) $500 e$ (D) $\frac{2}{1000e}$

Sol.

33. If a closed container of volume 200 lit. of O_2 gas (ideal gas) at 1 atm & 200 K is taken to planet. Find the pressure of oxygen gas at the planet at 821 K in same container

- (A) $\frac{10}{e^{100}}$ (B) $\frac{20}{e^{50}}$
(C) 1 atm (D) 2 atm

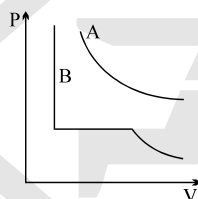
Sol.

Question No. 36 to 37 (2 questions)

For two gases A and B, P v/s V isotherms are drawn at T K as shown. T_A & T_B are critical temperatures of A & B respectively

34. Which of following is true?

- (A) $T_A < T < T_B$
(B) $T_A > T > T_B$
(C) $T_A > T_B > T$
(D) none of above



Sol.

35. The correct statement(s) is/are

- (I) Pressure correction term will be more negligible for gas B at T K.
(II) The curve for gas 'B' will be of same shape as for gas A if $T > T_B$
(III) Gas 'A' will show same P v/s V curve as of gas 'B' if $T > T_A$
(A) III only (B) II and III
(C) II only (D) All

Sol.

36. n moles of Helium gas are placed in a vessel of volume V lt. at T K. If V_I is free volume of Helium then diameter of He atom is

- (A) $\left[\frac{3}{2} \frac{V_I}{\pi N_A n} \right]^{\frac{1}{3}}$ (B) $\left[\frac{3(V - V_I)}{2 \pi N_A n} \right]^{\frac{1}{3}}$
(C) $\left[\frac{6(V - V_I)}{\pi N_A n} \right]^{\frac{1}{3}}$ (D) $\left[\frac{6V_I}{\pi N_A n} \right]^{\frac{1}{3}}$

Sol.

Exercise - III

(JEE ADVANCED)

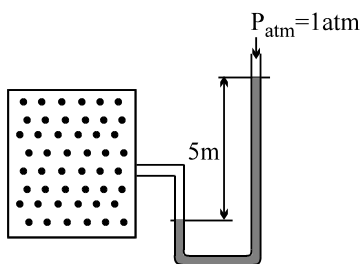
1. Automobile air bags are inflated with N_2 gas which is formed by the decomposition of solid sodium azide (NaN_3). The other product is Na - metal. Calculate the volume of N_2 gas at $27^\circ C$ and 756 Torr formed by the decomposition of 125 gm of solid azide.

Sol.

2. 3.6 gm of an ideal gas was injected into a bulb of internal volume of 8L at pressure P atm and temp T-K. The bulb was then placed in a thermostat maintained at $(T + 15)$ K. 0.6 gm of the gas was let off to keep the original pressure. Find P and T if mol weight of gas is 44.

Sol.

3. Calculate the number of moles of gas present in the container of volume 10 lit at 300 K. If the manometer containing glycerin shows 5m difference in level as shown in diagram.



Given: $d_{\text{glycerin}} = 2.72 \text{ gm/ml}$, $d_{\text{mercury}} = 13.6 \text{ gm/ml}$.

Sol.

4. A toy balloon originally held 1.0 gm of He gas and had a radius 10 cm. During the night, 0.25 gm of the gas effused from the balloon. Assuming ideal gas behaviour, under these constant P and T conditions, what was the radius of the balloon the next morning.

Sol.

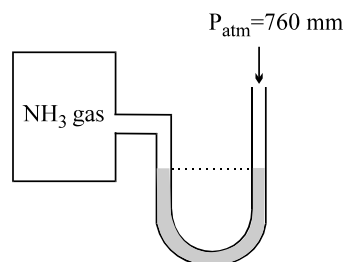
5. While resting, the average human male use 0.2 dm^3 of O_2 per hour at STP for each kg of body mass. Assume that all this O_2 is used to produce energy by oxidising glucose in the body. What is the mass of glucose required per hour by a resting male having mass 60 kg. What volume, at STP of CO_2 would be produced.

Sol.

6. An ideal gas is at a temperature of 200 K & at a pressure of 8.21 atm. It is subjected to change in volume by changing amount of the gas & a graph of n^2 vs V^2 (litre^2) is plotted. Is slope constant? If yes, calculate its value else justify why it is not constant.

Sol.

7. A manometer attached to a flask contains NH_3 gas have no difference in mercury level initially as shown in diagram. After the sparking into the flask, it have difference of 19 cm in mercury level in two columns. Calculate % dissociation of ammonia.



Sol.

8. 16 gm of O_2 was filled in a container of capacity 8.21 lit. at 300 K. Calculate
(i) Pressure exerted by O_2
(ii) Partial pressure of O_2 and O_3 if 50 % of oxygen is converted into ozone at same temperature.
(iii) Total pressure exerted by gases if 50% of oxygen is converted into ozone (O_3) at temperature 50 K.

Sol.

9. Calculate relative rate of effusion of SO_2 to CH_4 under given condition
(i) Under similar condition of pressure & temperature
(ii) Through a container containing SO_2 and CH_4 in 3:2 mass ratio
(iii) If the mixture obtained by effusing out a mixture ($n_{SO_2}/n_{CH_4} = 8/1$) for three effusing steps.

Sol.

10. A gas mixture contains equal number of molecules of N_2 and SF_6 , some of it is passed through a gaseous effusion apparatus. Calculate how many molecules of N_2 are present in the product gas for every 100 molecules of SF_6 .

Sol.

11. Two gases NO and O_2 were introduced at the two ends of a one metre long tube simultaneously (tube of uniform cross-section). At what distance from NO gas end, Brown fumes will be seen.

Sol.

12. At $20^\circ C$ two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with N_2 & other with H_2 . The N_2 balloon leaks to a pressure of $\frac{1}{2}$ atm in one hour. How long will it take for H_2 balloon to leak to a pressure of $\frac{1}{2}$ atm.

Sol.

13. Pure O_2 diffuses through an aperture in 224 sec, whereas mixture of O_2 and another gas containing 80 % O_2 Takes 234 sec to effuse out same volume What is molecular weight of the gas?

Sol.

- 14.** Find the number of diffusion steps required to separate the isotopic mixture initially containing some amount of H_2 gas and 1 mol of D_2 gas in a container of 3 lit capacity maintained at 24.6 atm & 27 °C to the final

$$\text{mass ratio } \left(\frac{w_{D_2}}{w_{H_2}} \right) \text{ equal to } \frac{1}{4}.$$

Sol.

- 15.**
- (a) How much H_2 (in mol) is needed to inflate a balloon of radius 3m to a pressure of 1 atmp in an ambient temp at 25° C at sea level.
- (b) What mass can the balloon lift at sea level, where the density of air is 1.22 Kg m^{-3} .
- (c) What would be the pay load if He were used instead of H_2 .

Sol.

- 16.** Calculate the pressure of a barometer on an aeroplane which is at an altitude of 10 Km. Assume the pressure to be 101.325 Kpa at sea level & the mean temperature 243 K. Use the average molar mass of air (80% N_2 , 20 % O_2)

Sol.

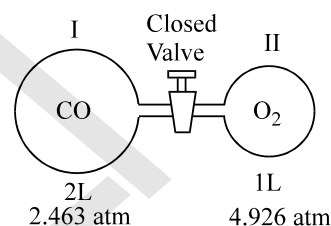
- 17.** What will be the temperature difference needed in a hot air balloon to lift 1.0 kg of mass? Assume that the volume of balloon is 100 m^3 , the temperature of ambient air is 25 °C, the pressure is 1 bar, and air is an ideal gas with an average molar mass of 29 g mol^{-1} (hot and cold both).

Sol.

- 18.** An iron cylinder contains helium at a pressure of 250 k pa and 27°C. The cylinder can withstand a pressure of $1 \times 10^6 \text{ pa}$. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not. [melting point of cylinder = 1800 k]

Sol.

- 19.** Determine final pressure after the valve is left opened for a long time in the apparatus represented in figure. Assume that the temperature is fixed at 300 K. Under the given conditions assume no reaction of CO & O_2 .



Sol.

- 20.** Calculate the temperature values at which the molecules of the first two members of the homologous series, C_nH_{2n+2} will have the same rms speed as CO_2 gas at 770 K. The normal b.p. of n-butane is 273 K. Assuming ideal gas behaviour of n-butane upto this temperature, calculate the mean velocity and the most probable velocity of its molecules at this temperature.

Sol.

- 21.** Calculate the temperatures at which the root mean square velocity, average velocity and most probable velocity of oxygen gas are all equal to 1500 ms^{-1} .

Sol.

- 22.** Calculate the fraction of N_2 molecules at 101.325 kPa and 300 K whose speeds are in the range of $u_{\text{mp}} - 0.005 u_{\text{mp}}$ to $u_{\text{mp}} + 0.005 u_{\text{mp}}$.

Sol.

- 23.** The density of mercury is 13.6 g/cm^3 . Estimate the b value.

Sol.

- 24.** Calculate from the vander waal's equation, the temperature at which 192 gm of SO_2 would occupy a vol. of 10 dm^3 at 15 atm pressure. [$a = 6.7 \text{ atm lit}^2 \text{ mol}^2$, $b = 0.0564 \text{ lit mol}^{-1}$]

Sol.

- 25.** The molar volume of He at 10.1325 MPa and 273 K is 0.011075 of its molar volume at 101.325 KPa at 273 K. Calculate the radius of helium atom. The gas is assumed to show real gas nature. Neglect the value of a for He.

Sol.

- 26.** N_2 molecule is spherical of radius 100 pm.
(a) What is the volume of molecules is one mole of a gas?
(b) What is the value of vander waal's constant b ?

Sol.

- 27.** The density of water vapour at 327.6 atm and 776.4 K is 133.2 gm/dm^3 . Determine the molar volume, V_m of water and the compression factor.

Sol.

- 28.** At 273.15 K and under a pressure of 10.1325 MPa, the compressibility factor of O_2 is 0.927. Calculate the mass of O_2 necessary to fill a gas cylinder of 100 dm^3 capacity under the given conditions.

Sol.

- 29.** 1 mole of CCl_4 vapours at 27°C occupies a volume of 40 lit. If Vander Waals constant are $24.6 \text{ L}^2 \text{ atm mol}^{-1}$ and 0.125 L mol^{-1} . Calculate compressibility factor under
 (a) Low pressure region
 (b) High Pressure region
 [Take $R = 0.082 \text{ lit-atm/mol/K}$]

Sol.

- 30.** The vander waals constant for O_2 are $a = 1.36 \text{ atm L}^2 \text{ mol}^{-2}$ and $b = 0.0318 \text{ L mol}^{-1}$. Calculate the temperature at which O_2 gas behaves, ideally for longer range of pressure.

Sol.

- 31.** The vander Waals constants for gases A, B and C are as follows

Gas	$a/\text{dm}^6 \text{ kPa mol}^{-2}$
$b/\text{dm}^3 \text{ mol}^{-1}$	
A	405.3
0.027	
B	1215.9
0.030	
C	607.95
0.032	

Which gas has (i) the highest critical temperature, (ii) the largest molecular volume, and (iii) most ideal behaviour around 600 K?

Sol.

- 32.** For a real gas (mol. mass = 30) if density at critical point is 0.40 g/cm^3 and its $T_c = \frac{2 \times 10^5}{821} \text{ K}$, then calculate Vander Waal's constant **a** (in $\text{atm L}^2 \text{ mol}^{-2}$).

Sol.

- 33.** One mole of a non linear triatomic gas is heated in a closed rigid container from 500°C to 1500°C . Calculate the amount of energy required if vibrational degree of freedom become effective only above 1000°C .

Sol.

- 34.** Calculate γ (ratio of C_p & C_v) for
 (a) Triatomic nonlinear gas at low temperature.
 (b) Triatomic linear gas at high temperature; assume that the contribution of vibrational degree of freedom is 50%.

Sol.

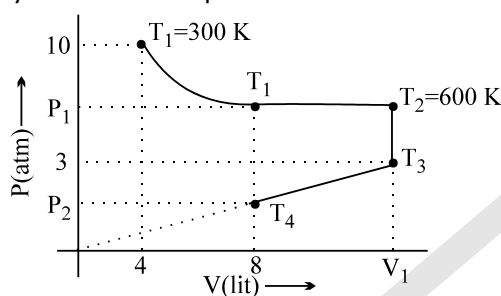
- 35.** A commercial cylinder contains 6.91 m^3 of O_2 at 15.18 MPa and 21°C . the critical constants for O_2 are $T_c = -118.4^\circ\text{C}$, $P_c = 50.1 \text{ atmp}$. Determine the reduced pressure and reduced temperature for O_2 under these conditions.

Sol.

36. At what temperature in $^{\circ}\text{C}$, the U_{rms} of SO_2 is equal to the average velocity of O_2 at 27°C .

Sol.

37. Fixed mass of a gas is subjected to the changes as shown in diagram, calculate T_3 , T_4 , P_1 , P_2 and V_1 as shown in diagram. Considering gas obeys $PV = nRT$ equation.



Sol.

38. A balloon containing 1 mole air at 1 atm initially is filled further with air till pressure increases to 3 atm. The initial diameter of the balloon is 1 m and the pressure at each state is proportion to diameter of the balloon. Calculate
- No. of moles of air added to change the pressure from 1 atm to 3 atm.
 - balloon will burst if either pressure increases to 7 atm or volume increases to $36\pi \text{ m}^3$. Calculate the number of moles of air that must be added after initial condition to burst the balloon.

Sol.

39. The composition of the equilibrium mixture ($\text{Cl}_2 \rightleftharpoons 2\text{Cl}$) which is attained at 1200°C is determined by measuring the rate of effusion through a pin hole. It is observed that at 1.8 mm Hg pressure, the mixture effuses 1.16 times as fast as Kr effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. [Kr = 84 a. m. u.]

Sol.

40. One mole of NH_4Cl (s) is kept in an open container & then covered with a lid. The container is now heated to 600 K where all NH_4Cl (s) dissociates into NH_3 & HCl (g). If volume of the container is 24.63 litres, calculate what will be the final pressure of gases inside the container. Also find whether the lid would stay or bounce off if it can withstand a pressure difference of 5.5 atm. Assume that outside air is at 300 K and 1 atm pressure.

Sol.

41. The compressibility factor for N_2 at -50°C and 800 atmp pressure is 1.95 and at 100°C and 200 atmp, it is 1.10. A certain mass of nitrogen occupied one litre at -50°C and 800 atmp. Calculate the volume occupied by the same quantity of N_2 at 100°C and 200 atmp.

Sol.

42. One mole of an ideal gas is subjected to a process in which $P = \frac{1}{8.21} V$ where P is in atm & V in litre. If the process is operating from 1 atm to finally 10 atm (no higher pressure achieved during the process) then what would be the maximum temperature obtained & at what instant will it occur in the process.

Sol.

43. A compound exists in the gaseous state both as a monomer (A) and dimer (A_2). The molecular weight of the monomer is 48. In an experiment, 96 g of the compound was confined in a vessel of volume 33.6 litres and heated to 273°C . Calculate the pressure developed, if the compound exists as a dimer to the extent of 50 per cent by weight, under these conditions. ($R = 0.082$)

Sol.

44. During one of his adventure, Chacha chaudhary got trapped in an underground cave which was sealed two hundred year back. The air inside the cave was poisonous, having some amount of carbon monoxide in addition to O_2 and N_2 . Sabu, being huge could not enter into the cave, so in order to save chacha choudhary be started sucking the poisonous air out of the cave by mouth. Each time, he filled his lunge with cave air and exhaled it out in the surroundings. In the mean time fresh air from surrounding effused into the cave till the pressure was again one atmosphere. Each time Sabu sucked out some air, the pressure in the cave dropped to half of its initial value of one atmosphere. If the initial sample of air from the cave contain 5% by volume CO. If the safe level of CO in the atmosphere is less than 0.001% by volume how many times does Sabu need to such out air in order to save Chacha chaudhary.

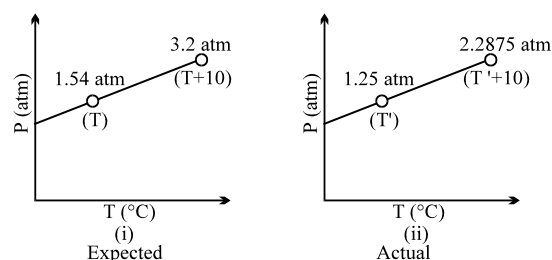
Sol.

45. You are told to prepare a closed experimental environment (a box) for student mice. The box volume will be 294 liters (about 10 ft^3) and the entire air volume will be changed every minute. The relative humidity of the air entering the box is to be controlled at 40% at 21°C . What weight of H_2O must be added to the flow of dry air per minute? (Equilibrium vapour pressure for H_2O at $21^\circ \text{C} \approx 19 \text{ torr}$). ($R = 0.082 \text{ liter atm mole}^{-1} \text{deg}^{-1}$ mol wt: $\text{H}_2\text{O} = 18$)

Sol.

46. A closed vessel of known volume containing known amount of ideal gaseous substance 'A' was observed for variation of pressure with temperature. The expected graph was to be like as in
(i) However actual observations revealed the graph to be like.
(ii) The deviation was attributed to polymerisation of gas molecules as $nA(g) \rightleftharpoons A_n(g)$. If it is known that the above reaction gives only 50% yield

- (a) Calculate the ratio of $\frac{n_{\text{experiment}}}{n_{\text{theoretical}}}$
(where $n_{\text{exp.}}$ = Total no. of gaseous mole acutally present $n_{\text{theoretical}}$ = Total no. of mole original taken)
(b) Find the value of n to which the gas A is being polymerised into



Sol.

47. A mixture of CH_4 & O_2 is used as an optimal fuel if O_2 is present in thrice the amount required theoretically for combustion of CH_4 . Calculate number of effusions steps required to convert a mixture containing 1 part of CH_4 in 193 parts mixture (parts by volume). If calorific value (heat evolved when 1 mole is burnt) of CH_4 is 100 cal/mole & if after each effusion 90% of CH_4 is collected, find out what initial mole of each gas in initial mixture required for producing 1000 cal of energy after processing. [Given $(0.9)^5 = 0.6$]

Sol.

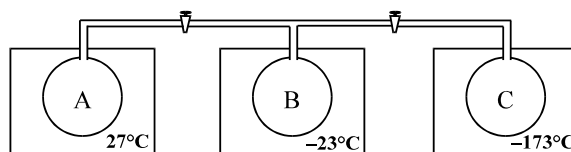
48. A 50 litre vessel is equally divided into three parts with the help of two stationary semi permeable membrane (SPM). The vessel contains 60 g H_2 gas in the left chamber, 160 g O_2 in the middle & 140 g N_2 in the right one. The left SPM allows transfer of only H_2 gas while the right one allows the transfer of both H_2 & N_2 . Calculate the final ratio of pressure in the three chambers.

Sol.

49. The apparatus shown consists of three temperature jacketed 1 litre bulbs connected by stop cocks. Bulb A contains a mixture of $\text{H}_2\text{O}(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{N}_2(\text{g})$ at 27°C and a total pressure of 547.2 mm Hg. Bulb B is empty and is held at a temperature -23°C . Bulb C is also empty and is held at a temperature of -173°C . The stopcocks are closed and the

volumes of lines connecting the bulbs is zero.
 Given: $\text{CO}_2(\text{g})$ converted into $\text{CO}_2(\text{s})$ at -78° ,
 $\text{N}_2(\text{g})$ converted into $\text{N}_2(\text{s})$ at -196°C & $\text{H}_2\text{O}(\text{g})$ converted into $\text{H}_2\text{O}(\text{s})$ at 0°C .

[Use $R = 0.08 \text{ atm-litre/mole-K}$]



- (a) The stopcock between A & B is opened and the system is allowed to come to equilibrium. The pressure in A & B is now 228 mmHg. What do bulbs A & B contain?
 (b) How many moles of H_2O are in system?
 (c) Both stopcocks are opened and the system is again allowed to equilibrium. The pressure throughout the system is 45.6 mmHg. What do bulbs A, B and C contain?
 (d) How many moles of N_2 are in the system?

Sol.

50. Find the critical constant (P_c , V_c and T_c) in terms of A and B, also find compressibility factor (z) for the following equation of state.

$$PV = RT - \frac{A}{V} + \frac{2B}{V^2}$$

where A and B are constant, P = pressure and V = molar volume.

Sol.

Exercise - IV**PREVIOUS YEAR QUESTIONS****LEVEL - I****JEE MAIN**

1. According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels – **[AIEEE-2003]**

- (A) In a straight line path
(B) With an accelerated velocity
(C) In a circular path
(D) In a wavy path

Sol.

2. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor of which of the following ? **[AIEEE-2004]**

- (A) $\frac{1}{2}$ (B) $\sqrt{(313/293)}$
(C) $\frac{313}{293}$ (D) 2

Sol.

3. In van der Waals equation of state of the gas law, the constant 'b' is a measure of - **[AIEEE-2004]**

- (A) intermolecular repulsions
(B) intermolecular attraction
(C) volume occupied by the molecules
(D) intermolecular collisions per unit volume

Sol.

4. Which one of the following statements is NOT true about the effect of an increase in temperature on the distribution of molecular speeds in a gas ? **[AIEEE-2005]**

- (A) The fraction of the molecules with the most probable speed increases
(B) The most probable speed increases
(C) The area under the distribution curve remains the same as under the lower temperature
(D) The distribution becomes broader

Sol.

5. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is - **[AIEEE-2007]**

- (A) $\frac{2}{3}$ (B) $\frac{1}{3} \times \frac{273}{298}$
(C) $\frac{1}{3}$ (D) $\frac{1}{2}$

Sol.

6. The no. of moles per litre in the equation $PV = nRT$ is expressed by - [AIEEE-2002]

- (A) $\frac{P}{RT}$ (B) $\frac{PV}{RT}$
(C) $\frac{RT}{PV}$ (D) None

Sol.

7. The correct value of R is - [AIEEE-2002]

- (A) $R = 0.082$ litre-atm
(B) $R = 8.314 \times 10^7$ erg $K^{-1} \text{ mol}^{-1}$
(C) $R = 2 K^{-1} \text{ mol}^{-1}$
(D) None

Sol.

8. If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K , how many moles of water are in the vapour phase when equilibrium is established? [AIEEE-2010]

(Given : Vapour pressure of H_2O at 300 is 3170 pa ; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

- (A) $1.27 \times 10^{-3} \text{ mol}$ (B) $5.56 \times 10^{-3} \text{ mol}$
(C) $1.53 \times 10^{-2} \text{ mol}$ (D) $4346 \times 10^{-2} \text{ mol}$

Sol.

9. 'a' and 'b' are Vander Waals' constant for gases. Chlorine is more easily liquefied than ethane because : [AIEEE-2011]

- (A) a and b for $\text{Cl}_2 > a$ and b for C_2H_6
(B) a and b for $\text{Cl}_2 < a$ and b for C_2H_6
(C) a for $\text{Cl}_2 < a$ for C_2H_6 but b for $\text{Cl}_2 > b$ for C_2H_6
(D) a for $\text{Cl}_2 > a$ for C_2H_6 but b for $\text{Cl}_2 < b$ for C_2H_6

Sol.

10. When r, P and M represent rate of diffusion, pressure and molecular mass, respectively, then the ratio of the rates of diffusion (r/r) of two gases A and B, is given as - [AIEEE-2011]

- (A) $(P_A/P_B)(M_B/M_A)^{1/2}$ (B) $(P_A/P_B)^{1/2}(M_B/M_A)$
(C) $(P_A/P_B)(M_B/M_A)^{1/2}$ (D) $(P_A/P_B)^{1/2}(M_B/M_A)$

Sol.

11. The molecular velocity of any gas is -
[AIEEE-2011]
(A) inversely proportional to absolute temperature
(B) directly proportional to square of temperature
(C) directly proportional to square root of temperature
(D) inversely proportional to the square root of temperature

Sol.

12. The compressibility factor for a real gas at high pressure is -
[AIEEE-2012]
(A) 1
(B) $1 + pb/RT$
(C) $1 - pb/RT$
(D) $1 + RT/pb$

Sol.

13. For gaseous state, if most probable speed is denoted by C^* , average speed by \bar{C} and mean square speed by C , then for a large number of molecules the ratios of these speeds are :

[Jee(Main) 2013, 3/120]

- (A) $C^* : \bar{C} : C = 1.225 : 1.128 : 1$
(B) $C^* : \bar{C} : C = 1.228 : 1.125 : 1$
(C) $C^* : \bar{C} : C = 1 : 1.128 : 1.225$
(D) $C^* : \bar{C} : C = 1 : 1.225 : 1.128$

Sol.

14. A gaseous hydrocarbon gives upon combustion 0.72 g of water and 3.08 g. of CO_2 . The empirical formula of the Hydrocarbon is :

[Jee(Main) 2013, 3/120]

- (A) C_2H_4 (B) C_3H_4
(C) C_6H_5 (D) C_7H_8

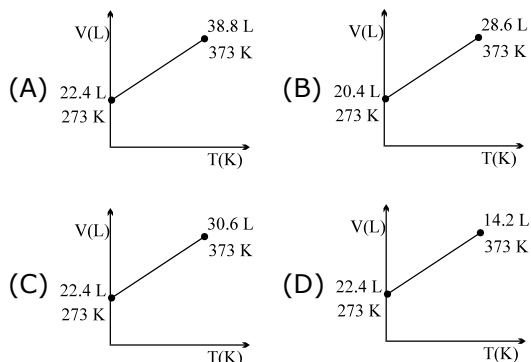
Sol.

LEVEL - II

JEE ADVANCED

1. Which one of the following V, T plots represents the behaviour of one mole of an ideal gas at one atm?

[JEE 2002]



Sol.

2. The density of the vapour of a substance at 1 atm pressure and 500 K is 0.36 Kg m^{-3} . The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.

[JEE 2002]

- (a) Determine
(i) mol. wt.; (ii) molar volume; (iii) compression factor (z) of the vapour and (iv) which forces among the gas molecules are dominating, the attractive or the repulsive
- (b) If the vapour behaves ideally at 1000 K, determine the average translational K.E. of a molecule.

Sol.

3. The average velocity of gas molecules is 400 m/sec. Calculate its (rms) velocity at the same temperature.

[JEE 2003]

Sol.

4. C_v value of He is always $3R/2$ but C_v value of H_2 is $3R/2$ at low temperature and $5R/2$ at moderate temperature and more than $5R/2$ at higher temperature explain in two to three lines.

[JEE 2003]

Sol.

5. Positive deviation from ideal behaviour takes place because of

[JEE 2003]

- (A) molecular attraction between atoms and $\frac{PV}{nRT} > 1$
- (B) molecular attraction between atoms and $\frac{PV}{nRT} < 1$
- (C) finite size of atoms and $\frac{PV}{nRT} > 1$
- (D) finite size of atoms and $\frac{PV}{nRT} < 1$

Sol.

6. For a real gas obeying van der Waal's equation a graph is plotted between PV_m (y-axis) and P (x-axis) where V_m is molar volume. Find y-intercept of the graph. [JEE 2004]

Sol.

- (A) for the gas A, $a = 0$ and its dependence on P is linear at all pressure
 (B) for the gas B, $b = 0$ and its dependence on P is linear at all pressure
 (C) for the gas C, which is typical real gas for which neither a nor $b = 0$. By knowing the minima and the point of intersection, with $Z = 1$, a and b can be calculated.
 (D) At high pressure, the slope is positive for all real gases A, B and C. [JEE 2006]

Sol.

7. The ratio of the rate of diffusion of helium and methane under identical condition of pressure and temperature will be
 (A) 4 (B) 2
 (C) 1 (D) 0.5 [JEE 2005]

Sol.

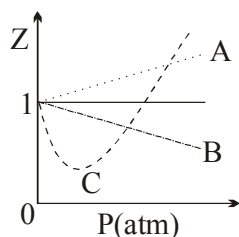
9. Match gases under specific conditions listed in Column I with their properties / laws in Column II. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS.

Column I**Column II**

- (A) Hydrogen gas ($P = 200$ atm, $T = 273$ K)
 (P) Compressibility factor $\neq 1$
 (B) Hydrogen gas ($P \sim 0$, $T = 273$ K)
 (Q) Attractive forces are dominant
 (C) CO_2 ($P = 1$ atm, $T = 273$ K)
 (R) $PV = nRT$
 (D) Real gas with very large molar volume
 (S) $P(V - nb) = nRT$ [JEE 2007]

Sol.

8. The given graph represents the variation of Z (compressibility factor = $\frac{PV}{nRT}$) versus P , for three real gases A, B and C. Identify the only incorrect statement.

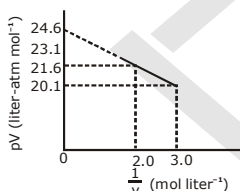


10. A gas described by van der Waals equation
[JEE 2008]

(A) behaves similar to an ideal gas in the limit of large molar volumes
(B) behaves similar to an ideal gas in the limit of large pressures
(C) is characterised by van der Waals coefficients that are dependent on the identity of the gas but are independent of the temperature
(D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

Sol.

11. For one mole of a van der Waals gas when $b = 0$ and $T = 300$ K, the PV vs. $1/V$ plot is shown below. The value of the van der Waals constant a (atm. liter² mol⁻²) is [JEE 2012]



- (A) 1.0 (B) 4.5
(C) 1.5 (D) 3.0

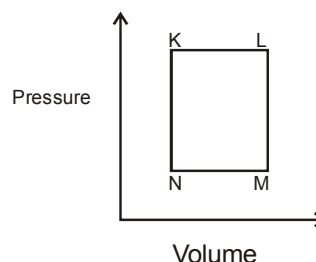
Sol.

12. The atomic masses of He and Ne are 4 and 20 a.m.u, respectively. The value of the de Broglie wavelength of He gas at -73°C is "M" times that of the de Broglie wavelength of Ne 727°C . M is : [JEE(ADVANCED)-2013, 4/120]

Sol.

Paragraph for Questions

A fixed mass 'm' of a gas is subjected to transformation of states from K to L to M to N and back to K as shown in the figure.



13. The succeeding operations that enable this transformation of states are

(A) Heating, cooling, heating, cooling
(B) Cooling, heating, cooling, heating
(C) Heating, cooling, cooling, heating
(D) Cooling, heating, heating, cooling

[JEE (ADVANCED)-2013,3/120]

Sol.

14. The pair of isochoric processes among the transformation of states is :

(A) K to L and L to M
(B) L to M and N to K
(C) L to M and M to N
(D) M to N and N to K

[JEE (ADVANCED)-2013,3/120]

Sol.

15. Two non-reactive monoatomic ideal gases have their atomic masses in the ratio 2 : 3. The ratio of their partial pressures, when enclosed in a vessel kept at a constant temperature, is 4 : 3. The ratio of their densities is [JEE (ADVANCED)-2013]

(A) 1 : 4 (B) 1 : 2
(C) 6 : 9 (D) 8 : 9

Sol.

Answers

Answer Ex-I

OBJECTIVE PROBLEMS (JEE MAIN)

1. D 2. D 3. B 4. B 5. B 6. D 7. C
 8. B 9. A 10. C 11. C 12. A 13. A 14. A
 15. A 16. C 17. C 18. A 19. B 20. C 21. A
 22. B 23. A 24. D 25. D 26. B 27. A 28. D
 29. B 30. C 31. B 32. A 33. C 34. B 35. B
 36. A 37. B 38. B 39. A 40. B 41. C 42. D
 43. A 44. A 45. A 46. C 47. A 48. C 49. C
 50. C

Answer Ex-II

OBJECTIVE PROBLEMS (JEE ADVANCED)

1. C 2. B 3. B 4. directly proportional 5. $B = \left(b - \frac{\alpha}{RT} \right)$
 6. 0.492 atmp ; 0.246 atmp 7. C 8. 123
 9. 6.46 atmp L² mol⁻² 10. -173°C , 0.82 L 11. XeF₆
 12. C 13. B 14. C 15. Both statements are correct
 16. D 17. 1.2544 atmp L² mol⁻² 18. A,C 19. A 20. A,B
 21. A,B 22. A,C 23. A,D 24. B,C 25. B,D
 26. (A) R, (B) S, (C) P, (D) Q 27. (A) S; (B) R, (C) Q; (D) P 28. D
 29. C 30. A 31. B 32. D 33. A
 34. A 35. C 36. C

Answer Ex-III**SUBJECTIVE PROBLEMS (JEE ADVANCED)**

1. 71.4 L
2. $P = 0.062 \text{ atm}$, $T = 75 \text{ K}$
3. 0.94 mole
4. 9.08 cm
5. 16.07 gm ; 12 dm³
6. $\frac{1}{4}$
7. 25 %
8. (i) 1.5 atm; (ii) $O_2 = 0.75 \text{ atm}$, $O_3 = 0.5 \text{ atm}$; (iii) 0.208 atm
9. (i) $\frac{1}{2}$; (ii) $\frac{3}{16}$; (iii) $\frac{1}{2}$
10. 228
11. 50.8 cm
12. 16 min
13. 46.6
14. 4
15. $4.62 \times 10^3 \text{ moles}$, 128.79 Kg, 119.55Kg
16. 25.027 Kpa
17. 2.53°C
18. Yes
19. 3.284 atm
20. 280 K, 525 K, $3.157 \times 10^2 \text{ m/sec}$, $2.798 \times 10^2 \text{ m/sec}$
21. $T_{\text{RMS}} = 2886 \text{ K}$, $T_{\text{av}} = 3399 \text{ K}$, $T_{\text{mp}} = 4330 \text{ K}$
22. 8.303×10^{-3}
23. 58.997 cm³
24. 350.5°C
25. $r = 1.33 \times 10^{-8}$
26. (a) $2.52 \times 10^{-3} \text{ l mol}^{-1}$, (b) $10.08 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$
27. Molar vol = 0.1353 L/mol; $Z = 0.6957$
28. 15.40 kg
29. (a) 0.975; (b) 1.003
30. 521 K
31. (i) B, (ii) C, (iii) A
32. 1.6875
33. 4500 RJ
34. (a) 1.333, (b) 1.222
35. $\pi = 2.99$, $\theta = 1.90$
36. 236.3°C
37. (i) $P_1 = 5 \text{ atm}$; (ii) $T_3 = 360 \text{ K}$; (iii) $V_1 = 16 \text{ lit.}$; (iv) $P_2 = 1.5 \text{ atm}$; (v) $T_4 = 90 \text{ K}$
38. $P \propto d$; $P = kd$ & $k = \frac{1 \text{ atm}}{1 \text{ meter}}$; (a) 80; (b) 1295 moles
39. 0.137
40. 6 atm, No
41. 3.77 L
42. 10,000 K
43. 2 atmp
44. 13
45. 2.2 g
46. (a) 0.625, (b) 4
47. 10 Steps, 27.78 mol CH₄, 5333.3 mol O₂
48. 4 : 7 : 5

49. (a) Bulb A : $N_2(g), CO_2(g)$
 Bulb B: $N_2(g), CO_2(g), H_2O(s)$
 (b) No. of mole of $H_2 = 0.0025$
 (c) Bulb A : $N_2(g)$
 Bulb B : $N_2(g), H_2O(s)$
 Bulb C : $N_2(g), CO_2(s)$
 (d) Total no. of mole of N_2 in system = 0.013

50. $V_C = \frac{6B}{A}, T_C = \frac{A^2}{6RB}, P_C = \frac{A^3}{108B^2}, \text{compressibility factor} = \frac{P_C V_C}{RT_C} = \frac{1}{3}$

Answer Ex-IV**PREVIOUS YEARS PROBLEMS****SECTION – A****JEE MAIN**

1. A 2. C 3. C 4. A 5. C 6. A 7. B
 8. A 9. D 10. A 11. C 12. B 13. C 14. D

SECTION-B**JEE ADVANCED**

1. C
 2. (a) (i) 18.1 g/mol , (ii) 50.25 L mol⁻¹ , (iii) 1.224 , (iv) repulsive, (b) 2.07×10^{-20} J
 3. 434.17 m/sec
 4. Since H_2 is diatomic and He is monoatomic degree of freedom for mono is 3 and only translational but for diatomic, vibrational and rotational are also to be considered
 5. C 6. RT 7. B 8. B 9. (A) P, S; (B) R; (C) P, Q; (D) R
 10. A,C,D 11. C 12. 5 13. C 14. B 15. D